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Intramolecular Oxidative Cyclization of Alkenes and Nitriles with Nickel(0)

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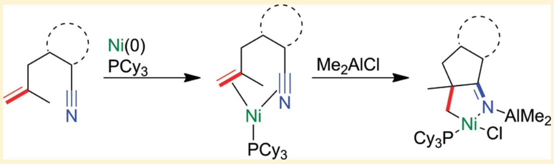
S Supporting Information



ABSTRACT: The use of Me_2AlCl as an additive was found to allow the oxidative addition of the Ar−CN bond in 2-(2-methylallyl)benzonitrile on nickel(0) in the presence of P^nBu_3, giving a *trans*-arylnickelcyanide complex. In contrast, in the presence of PCy_3, the intramolecular oxidative cyclization on nickel(0) took place to afford a nickeladihydropyrrole. Without the addition of Me_2AlCl, the quantitative generation of an η^2:η^2-5-ene-nitrile Ni(0) species, which was definitely converted to the nickeladihydropyrrole after treatment with Me_2AlCl, was observed. In addition, TfOH also promoted the oxidative cyclization of the η^2:η^2-5-ene-nitrile complex to yield the corresponding five-membered aza-nickelacycle. A similar intramolecular oxidative cyclization occurred when 2-allylbenzonitrile was used in the presence of a Lewis acid, such as Me_2AlCl, Me_2AlOTf, and Me_3SiOTf, or of TfOH to give the corresponding nickeladihydropyrroles in quantitative yield. The molecular structures of a series of nickeladihydropyrroles were unambiguously determined by means of X-ray crystallography. The nickeladihydropyrrole derived from (2-methylallyl)benzonitrile and TfOH was found to react with $HSiMe_2Ph$ at 80 °C to furnish a silanamine derivative. The reaction was expanded to a Ni(0)/PCy_3/TfOH-catalyzed coupling reaction of 5-ene-nitrile and $HSiMe_2Ph$, yielding the corresponding silanamine in 84% yield.

INTRODUCTION

Oxidative cyclization of two π-components with nickel(0) species is an efficient method for the generation of a heteronickelacycle, which has been proposed as a key reaction intermediate in nickel-catalyzed multicomponent coupling reactions as well as [2 + 2 + 2] cycloaddition reactions to give heterocycles.[1] Earlier studies reported by Hoberg had focused on the formation of heteronickelacycles by oxidative cyclization with nickel(0) complexes, including carbon dioxide[2] or isocyanate[3] as one π-component. In recent studies, our group reported the formation of five-membered heteronickelacycles by oxidative cyclization of a carbon−carbon unsaturated bond and a carbon-heteroatom double bond with nickel(0), such as alkene−aldehyde, alkene−ketone, diene−aldehyde, diene−ketone, alkyne−aldehyde or alkyne−imine.[4] However, the oxidative cyclization of nitriles and unsaturated hydrocarbons with nickel is very rare (Scheme 1).[5] The occurrence of the oxidative cyclization of alkyne and nitrile with nickel(0) has only been inferred from the formation of an enone by the protonolysis of a reaction mixture of diphenylacetylene and benzonitrile with Ni(0).[5a] Louie and co-workers proposed that, in the Ni/NHC-catalyzed formation of pyridines from alkynes and nitriles, a nickelapyrrole intermediate would be generated through the oxidative cyclization of an alkyne and a nitrile with nickel(0).[5b,c] The reason for the rareness is that the oxidative addition of the C−CN bond of η^2-nitrile Ni(0) complexes competes against oxidative cyclization (Scheme 1).[6−13] In fact, some nickel-catalyzed reactions involving a C−CN bond cleavage of nitriles as a key reaction step have appeared in the last decades.[14−18]

When all transition metal complexes are included, a significant number of aza-metalacycles generated by oxidative cyclization of nitriles and carbon−carbon unsaturated compounds has been discovered.[19−27] To the best of our knowledge, earlier research on a series of dihydrotitanapyrroles, generated by the reaction of (η^5-C_5Me_5)Ti(η^2-C_2H_4) with an equimolar amount of nitriles, was conducted by Bercaw et al.[19] Buchwald and co-workers, around the same time, engaged in the study on zirconocene-benzyne and zirconocene-alkyne complexes, both of which were found to react with nitriles to give the corresponding zirconapyrroles.[20] The first structural determination of the aza-metallacycle, derived from the oxidative cyclization of the *in situ* generated Cp_2Zr(η^2-benzyne) species with butyronitrile, was also achieved.[20c] They also demonstrated that treatment of a zirconocene-cyclobutene complex with nitriles gave the corresponding aza-zirconacycles,[21] and a related aza-zirconacycle derived from a zirconocene-cyclobutadiene complex with pivalonitrile was structurally determined by Sharp et al.[21b] The formation of five-membered aza-zirconacycle derivatives was also reported by the use of dialkylzirconocenes, such as Cp_2ZrBu_2 and Zp_2ZrEt_2, as a synthetic precursor.[22] Furthermore, Fagan and Nugent showed that an aza-zirconacyclopentadiene complex, generated by the intramolecular cyclization with 1-cyano-5-heptyne, reacted with S_2Cl_2 to give an isothiazole,[23]

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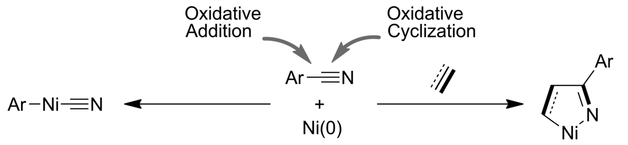
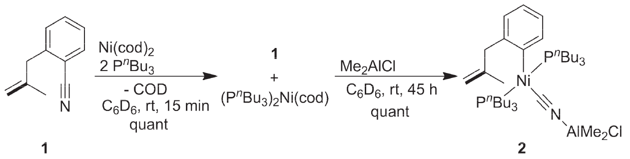
Scheme 1. Two Possible Reactions of Nitrile with Nickel(0)



Scheme 2. Oxidative Addition of 1 to Nickel(0)



while aza-zirconacycles were well-known to be hydrolyzed to yield the corresponding carbonyl compounds. A few aza-metallacycles containing a Group 4 metal, in addition, have also been synthesized and structurally well-defined by means of X-ray diffraction analysis.[24]

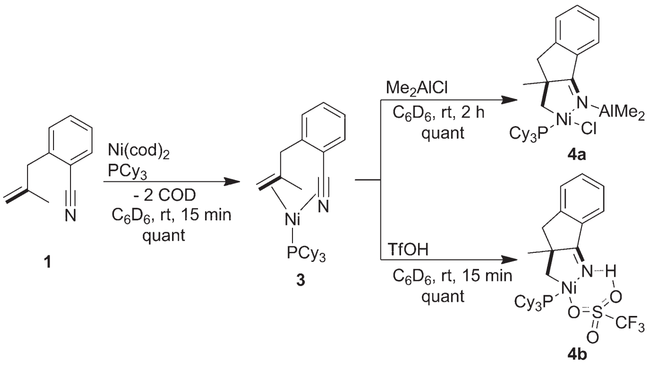
Although the number of aza-metallacycles generated by the oxidative cyclization of nitriles and carbon—carbon unsaturated compounds with Group 4 metal is not relatively small, as mentioned above, the corresponding aza-metallacycles containing except for Group 4 metals are still rare. Strickler and Wigley inferred the generation of aza-tantalacyclopentadiene in the course of the reaction of tantalum-tolan complex with nitrile.[25] Legzdins and co-workers proposed the formation of aza-tungstenacyclopentadienyl intermediate from the reaction of an η^2-PhCCH tungsten complex with acetonitrile.[26] Roesky et al. reported a unique reactivity of cyclopropane analogues of aluminum bearing a bulky β-diketiminato ligand toward benzonitrile to yield an aza-aluminacyclopentadiene, the molecular structure of which was definitely confirmed by X-ray diffraction study.[27] Here, we report the intramolecular oxidative cyclization of nitrile and alkene with nickel(0), promoted by a Lewis or Brønsted Acid. In addition, we observed that the aza-nickelacycle could act as a key intermediate in a catalytic reaction.

RESULTS AND DISCUSSION

The reaction of 2-(2-methylallyl)benzonitrile (**1**) with Ni(cod)$_2$ and P^{n}Bu$_3$ in C$_6$D$_6$ gave a mixture of **1** and Ni(cod)(P^{n}Bu$_3$)$_2$. The addition of Me$_2$AlCl to the reaction mixture promoted the oxidative addition of the aryl-CN bond to nickel(0) at room temperature to yield an arylnickelcyanide complex (**2**) quantitatively (Scheme 2). The oxidative addition of an Ar—CN bond to nickel(0) promoted by Lewis acids has been reported.[6b,14,28] We also reported the oxidative addition of an Ar—CN bond of 2-(3-methyl-3-butenyl)benzonitrile by the addition of Me$_2$AlCl and suggested that the coordination ability of the nitrile group was enhanced by coordination of nitrile nitrogen to Me$_2$AlCl.[14c] Insertion of the intramolecular alkene into the nickel-arene bond in **2** did not occur, even at 60 °C for 72 h, although the corresponding complex derived from 2-(3-methyl-3-butenyl)benzonitrile underwent insertion under the same reaction conditions.[14c]

In the presence of PCy$_3$, the reaction of **1** with Ni(cod)$_2$ gave an η^2:η^2-5-ene-nitrile Ni(0) complex (**3**) quantitatively.

Scheme 3. Oxidative Cyclization of 3 Promoted by either Me$_2$AlCl or TfOH



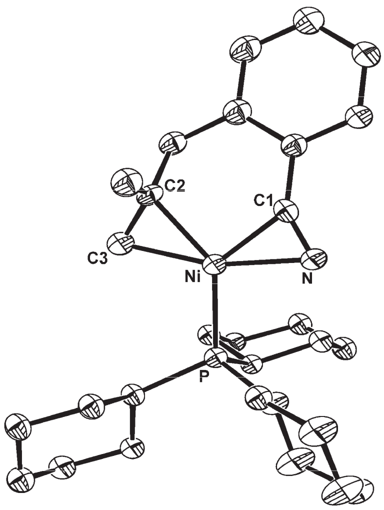


Figure 1. ORTEP drawing of **3** with thermal ellipsoids at the 30% probability level. One of the two independent molecules in a unit cell of **3** is depicted. H atoms are omitted for clarity.

The molecular structure was determined by X-ray crystallography (Scheme 3, Figure 1). The coordination geometry of the nickel center in **3** appeared to be a Y-shaped trigonal-planar structure, in which the midpoints of the carbon—carbon double and carbon—nitrile triple bonds are assumed to serve as a coordination center. The C1—N and C2—C3 bond distances of 1.215(7) and 1.390(9) Å, respectively, were slightly longer than those observed in uncoordinated PhCN (1.168(3) Å)[29] and ethylene (1.336(3) Å),[30] due to the contribution of back-donation from the nickel(0) center. The η^2:η^2-coordination structure of **3** was also observed in solution, as evidenced by the upfield shift of the ^{13}C resonances attributable to the coordinating alkene and nitrile moieties (δ_C 154.9, 76.9, and 50.4 for C1, C2, and C3, respectively).

The addition of Me$_2$AlCl to a solution of **3** promoted oxidative cyclization to give a nickeladihydropyrrole (**4a**) quantitatively (Scheme 3). The formation of a new carbon—carbon bond between C1 and C2 (1.508(3) Å) could be observed in the molecular structure of **4a** revealed by X-ray crystallography (Figure 2). Simultaneous formation of Ni—N and Ni—C3 bonds (1.9164(14) and 1.958(2) Å, respectively) was also confirmed, and these bond lengths were consistent with those observed in a

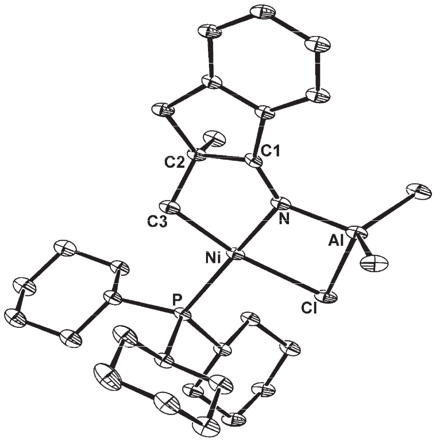


Figure 2. ORTEP drawing of **4a** with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity.

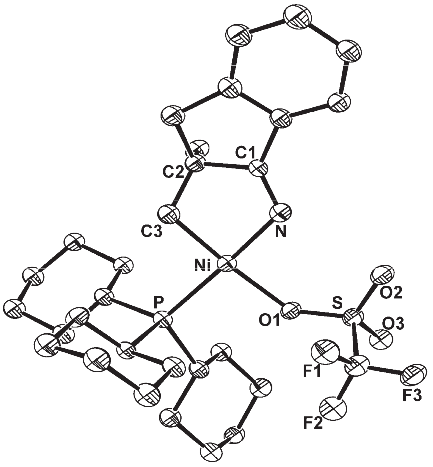


Figure 3. ORTEP drawing of **4b** with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity.

structurally well-defined seven-membered aza-nickelacycle.[4d] The chloride atom of **4a** bridged between the nickel and aluminum atoms, so Me_2AlCl served not only as a Lewis acid to promote the oxidative cyclization of **3**, but also as a Lewis base to stabilize the square-planar geometry of the Ni(II) center in **4a** by coordination of the chloride atom to the nickel.[31] The important role of Lewis acid in promoting oxidative addition has already demonstrated by our group[4a,b,h] and other groups.[32] The C2–C3 and C1–N bond distances (1.534(2) and 1.274(2) Å, respectively) of **4a** were nearly identical to the typical lengths of carbon–carbon single and carbon–nitrogen double bonds, respectively.

The oxidative cyclization of **3** was also promoted by the addition of a stoichiometric amount of TfOH. A nickeladihydropyrrole (**4b**) was isolated in 97% yield and its molecular structure was determined by X-ray crystallography (Scheme 3, Figure 3). Similar to the chloride atom in **4a**, one of the oxygen atoms in the trifluoromethanesulfonate group of **4b** coordinated to the nickel center to allow it to adopt a 16-electron, square-planar geometry. The C1–C2 and Ni–N bond lengths of 1.504(13) and 1.284(11) Å, respectively, of **4b** were almost equal to those observed in **4a**. The interatomic distance between the N and O2 atoms (2.99 Å) suggests the existence of the hydrogen bond. The ^1H NMR spectrum of **4b** exhibited a broad singlet at δ 8.95 ppm, assignable to the hydrogen adjacent to the nitrogen atom.

As mentioned above, in the reaction of Ni(0) with **1**, the nature of phosphine ligands apparently influenced a choice of the two reaction courses, the oxidative addition of the Ar–CN bond in the presence of P^nBu_3 or the oxidative cyclization in the presence of PCy_3. However, the factor determining the reaction course was found to depend on not only the nature of ligands but also the chain length of ene-nitrile. Treating of 2-(3-methyl-3-butenyl)benzonitrile (**5**) with $Ni(cod)_2$ and PCy_3 in the presence of Me_2AlCl followed by protolysis resulted in the quantitative formation of an intramolecular carbocyanation product (**6**), which was the product via the oxidative addition of the Ar–CN bond (Scheme 4).[14c] Monitoring of the initial stage of the reaction before adding Me_2AlCl by means of NMR spectroscopy indicated the formation of two Ni(0) intermediates (**A** and **B**). These results clearly show that PCy_3 promotes predominantly the oxidative addition of the Ar–CN bond when **5**, which has a longer alkyl chain than **1**, is employed as a substrate.

In a similar manner, the reaction of 2-allylbezonitrile (**7**) with $Ni(cod)_2$ in the presence of PCy_3 led to the qualitative formation of the corresponding η^2:η^2-5-ene-nitrile Ni(0) complex (**8**) (Scheme 5). The molecular structure of **8** was unambiguously determined by means of X-ray crystallography, and the ORTEP drawing is shown in Figure 4. The coordination geometry of the nickel center as well as the C1–N and C2–C3 bond distances (1.204(2) and 1.401(3) Å, respectively) of **8** were consistent with those observed in the analogous η^2:η^2-5-ene-nitrile complex **3**. The resonance assignable to the coordinating PCy_3 ligand appeared as a singlet at δ 37.4 in the $^{31}P\{^1H\}$ NMR spectrum of **8**.

In the presence of Me_2AlCl, the oxidative cyclization of **8** occurred faster than that of **3** at room temperature to quantitatively yield an aza-nickelacycle (**9a**) (Scheme 5). In addition, the oxidative cyclization of **8** proceeded smoothly with the addition of Me_2AlOTf, resulting in the quantitative formation of the corresponding nickeladihydropyrrole (**9b**). X-ray diffraction studies of **9a** and **9b** clearly demonstrated the formation of the five-membered Ni–N–C1–C2–C3 framework (Figure 5). In spite of the similar five-membered framework, however, the Ni–N bond distance of **9b** (1.9949(19) Å) was slightly longer than that found in **4a**–**b** (1.9164(14) and 1.905(9) Å, respectively) and **9a** (1.930(3) Å). The same coordination mode of Me_2AlOTf to the five-membered heteronickelacycle was previously demonstrated in the reaction of ^tBuCHO and diphenylacetylene with nickel(0).[4h]

As with the reaction of **3** with TfOH, the addition of an equimolar amount of TfOH allowed the oxidative cyclization of **8** to yield a nickeladihydropyrrole (**9c**) analogous to **4b** in quantitative yield (Scheme 6). In contrast, treatment of **8** with CH_3COOH instead of TfOH did not promote the corresponding oxidative cyclization. The interatomic distance between the N and O2 atoms (2.94 Å) was almost equal to that observed in **4b** (*vide supra*), which also suggested the existence of the hydrogen bond (Figure 6). A broad singlet at δ 9.13 ppm observed in the ^1H NMR spectrum of **9c** was assigned to the OH group hydrogen-bonding to the nitrogen atom. Furthermore, similar oxidative cyclization was promoted by the use of Me_3SiOTf, affording **9d** in a quantitative yield (Scheme 6). The X-ray diffraction study of **9d** clearly showed that the Si–O bond in

Table 1. Crystallographic Data of 3, 4a–b, 8, and 9a–d ^{a,b}

complex	3	4a	4b	8
empirical formula	$C_{29}H_{44}NNiP$	$C_{31}H_{50}AlClNNiP$	$C_{30}H_{45}F_3NNiO_3PS$	$C_{28}H_{42}NNiP$
formula weight	496.33	588.83	646.41	482.31
color, description	yellow, block	orange, block	yellow, block	yellow, block
temperature, K	123(2)	123(2)	123(2)	123(2)
cryst. System	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2/c$ (#13)	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P2_1/c$ (#14)
a, Å	14.7687(12)	10.4287(5)	9.1579(8)	8.3374(5)
b, Å	12.0964(10)	12.2964(8)	22.3334(17)	33.3279(17)
c, Å	30.477(3)	14.4467(8)	15.0975(14)	9.2706(6)
α, deg		66.299(2)		
β, deg	101.537(2)	80.093(2)	93.729(3)	99.118(2)
γ, deg		67.103(2)		
volume, Å^3	5334.6(8)	1562.40(15)	3081.3(5)	2543.4(3)
Z	8	2	4	4
calculated density, Mg m^{-3}	1.236	1.252	1.393	1.260
$2\theta_{max}$, deg	50.7	54.9	50.0	61.0
limiting indices	$-17 \le h \le 16, -14 \le k \le 14, -36 \le l \le 36$	$-12 \le h \le 13, -15 \le k \le 15, -18 \le l \le 15$	$-10 \le h \le 10, -26 \le k \le 25, -17 \le l \le 17$	$-11 \le h \le 11, -46 \le k \le 45, -13 \le l \le 13$
absorption coefficient, mm^{-1}	0.804	0.806	0.799	0.841
max. and min transmission	0.856 (max)/0.795 (min)	0.739 (max)/0.602 (min)	0.857 (max)/0.741 (min)	0.679 (max)/0.632 (min)
F(000)	2144	632	1368	1040
crystal size, mm	0.30 × 0.20 × 0.20	0.70 × 0.50 × 0.40	0.40 × 0.30 × 0.20	0.60 × 0.60 × 0.50
goodness-of-fit on F^2	1.013	1.106	1.360	1.035
reflections collected/unique	27633/9523 [R(int) = 0.141]	15159/7028 [R(int) = 0.028]	23332/5312 [R(int) = 0.127]	30975/7653 [R(int) = 0.059]
no. of variables	592	329	364	287
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0768, 0.1602	0.0338, 0.0862	0.1193, 0.3070	0.0463, 0.1090
$R1$, $wR2$ (all data)	0.1611, 0.1984	0.0390, 0.0897	0.1582, 0.3437	0.0688, 0.1249
residual electron density, e Å^{-3}	1.079 (max), −0.675 (min)	0.838 (max), −0.417 (min)	2.310 (max), −0.750 (min)	1.207 (max), −0.532 (min)

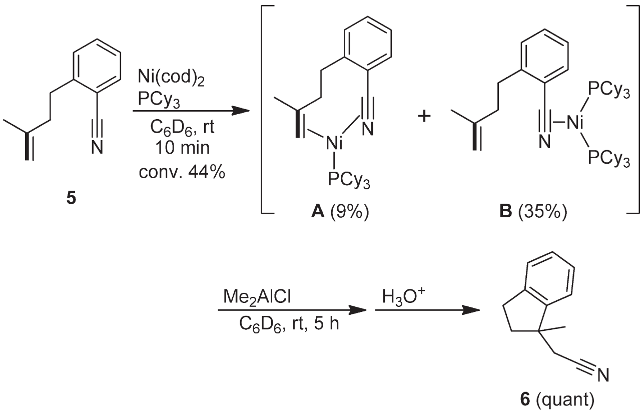
complex	9a	9b	9c	9d
empirical formula	$C_{30}H_{48}AlClNNiP$	$C_{31}H_{48}AlF_3NNiO_3PS$	$C_{29}H_{43}F_3NNiO_3PS$	$C_{32}H_{51}F_3NNiO_3PSSi \cdot C_7H_8$
formula weight	574.80	688.42	632.38	796.70
color, description	yellow, block	orange, block	yellow, block	red, block
temperature, K	296(2)	123(2)	123(2)	123(2)
cryst. System	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P\bar{1}$ (#2)
a, Å	16.6868(13)	12.1333(9)	10.5957(5)	9.4279(7)
b, Å	10.2681(8)	15.7000(11)	15.5640(8)	14.2349(10)
c, Å	18.9795(17)	19.0696(12)	18.4190(10)	15.7794(10)
α, deg				74.939(2)
β, deg	113.851(2)	109.714(2)	104.836(2)	87.102(2)
γ, deg				84.712(2)
volume, Å^3	2974.2(4)	3419.7(4)	2936.2(3)	2035.5(2)
Z	4	4	4	2
calculated density, Mg m^{-3}	1.284	1.337	1.431	1.300
$2\theta_{max}$, deg	57.0	61.0	50.0	50.0
limiting indices	$-22 \le h \le 22, -13 \le k \le 13, -25 \le l \le 25$	$-17 \le h \le 17, -22 \le k \le 22, -26 \le l \le 27$	$-12 \le h \le 12, -18 \le k \le 18, -21 \le l \le 21$	$-11 \le h \le 11, -16 \le k \le 16, -18 \le l \le 18$
max. and min transmission	0.920 (max)/0.849 (min)	0.865 (max)/0.662 (min)	0.921 (max)/0.851 (min)	0.830 (max)/0.738 (min)
absorption coefficient, mm^{-1}	0.845	0.748	0.837	0.646
F(000)	1232	1456	1336	848
crystal size, mm	0.20 × 0.20 × 0.10	0.60 × 0.50 × 0.20	0.20 × 0.20 × 0.10	0.50 × 0.30 × 0.30
goodness-of-fit on F^2	1.110	1.082	1.072	1.053
reflections collected/unique	30573/7492 [R(int) = 0.086]	41324/10380 [R(int) = 0.054]	15731/5043 [R(int) = 0.088]	16182/7146 [R(int) = 0.064]

Table 1. Continued

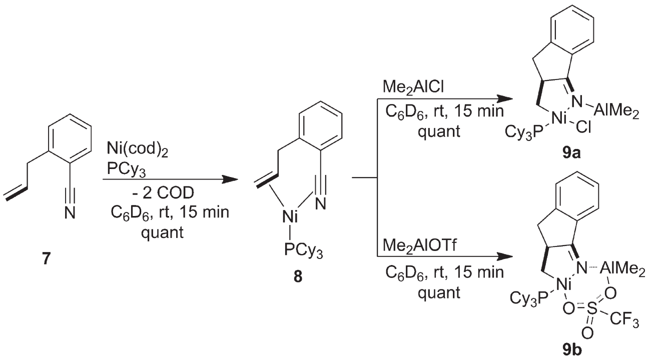
complex	9a	9b	9c	9d
no. of variables	318	382	354	456
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0643, 0.1587	0.0460, 0.1070	0.0574, 0.1097	0.0547, 0.1355
$R1$, $wR2$ (all data)	0.1142, 0.2048	0.0707, 0.1207	0.1208, 0.1514	0.0716, 0.1498
residual electron density, e Å^{-3}	1.203 (max), −1.102 (min)	0.871 (max), −0.630 (min)	0.901 (max), −0.826 (min)	0.863 (max), −0.598 (min)

[a] $R1 = (\Sigma||Fo| - |Fd||)/\Sigma|Fo|$. [b] $wR2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma(wFo^4)]^{1/2}$; the function minimized: $w(Fo^2 - Fc^2)^2$.

Scheme 4. Reaction of 5 with Ni(0) in the Presence of PCy_3 and Me_2AlCl



Scheme 5. Oxidative Cyclization of 8 Promoted by Me_2AlX (X = Cl and OTf)



Me_3SiOTf was completely cleaved (Figure 6).[4a] As a result, unlike the other nickeladihydropyrroles **4b**, **9b**, and **9c**, the triflate in **9d** was coordinated to the nickel center as a mono-anionic monodentate ligand. In addition, a new Si−N bond was formed with a distance of 1.783(3) Å, whereas the N−C1 bond distance of 1.282(4) Å was the typical length of the C═N double bond. Therefore, the slight elongation of the Ni−N bond distance (1.997(3) Å) may be due to the formation of a Ni−N coordination bond.

Finally, the reaction of aza-nickelacycles with $HSiMe_2Ph$ was examined. Only **4b** was found to react with $HSiMe_2Ph$ at 80 °C in the presence of **1** to afford a silanamine derivative (**10**) in 81% yield (Scheme 7). However, in the absence of **1**, the silanamine **10** was not generated. This observation suggests that the existence of **1**, which has alkene and nitrile moieties that can coordinate to stabilize a Ni(0) species, might play an important role in this transformation, and that this stoichiometric formation of **10** from **1** and $HSiMe_2Ph$ via the nickeladihydropyrrole intermediate **4b** may be applied to the catalytic reaction. In fact, in the presence of $Ni(cod)_2$ and PCy_3 (10 mol % each) and TfOH (5 mol %), the reaction of $HSiMe_2Ph$ with **1** at 80 °C afforded **10** in 84% isolated yield (Scheme 8). As shown in Scheme 8, this catalytic reaction probably proceeded via the TfOH-promoted intramolecular oxidative cyclization of **1** with Ni(0), followed by hydrosilylation of the resulting Ni−N bond.

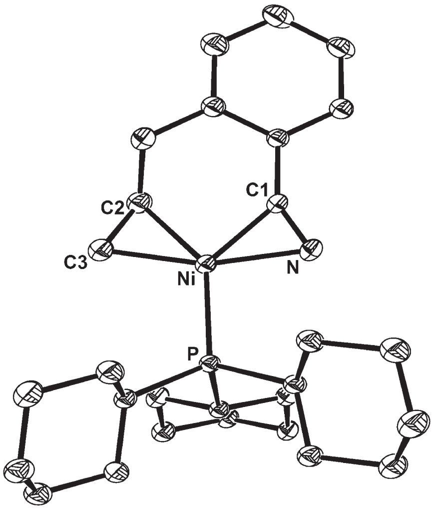


Figure 4. ORTEP drawing of **8** with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity.

In conclusion, we demonstrated the Me_2AlCl-mediated intramolecular oxidative cyclization of 5-ene-nitrile with nickel(0) in the presence of PCy_3 as a ligand. Me_2AlCl played two important roles for the oxidative cyclization of 5-ene-nitrile, as a Lewis acid to promote the cyclization reaction and as a Lewis base to stabilize the resulting square-planner structure of the Ni(II) product. In contrast, when P^nBu_3 was used as a ligand, oxidative addition of the C−CN bond of the 5-ene-nitrile to Ni(0) took place under the same reaction conditions. The oxidative cyclization of 5-ene-nitrile was also observed with the addition of a Brønsted acid such as TfOH. The nickeladihydropyrrole product reacted with $HSiMe_2Ph$ to give a silanamine derivative in the presence of 5-ene-nitrile. We also achieved the catalytic formation of silanamine. This catalytic reaction is the first example of a Ni(0)-catalyzed transformation reaction obviously involving the formation of an aza-nickelacycle intermediate via the oxidative cyclization of a nitrile and a carbon−carbon unsaturated molecule.

■ EXPERIMENTAL SECTION

General. All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or drybox techniques. ^1H, ^{31}P and

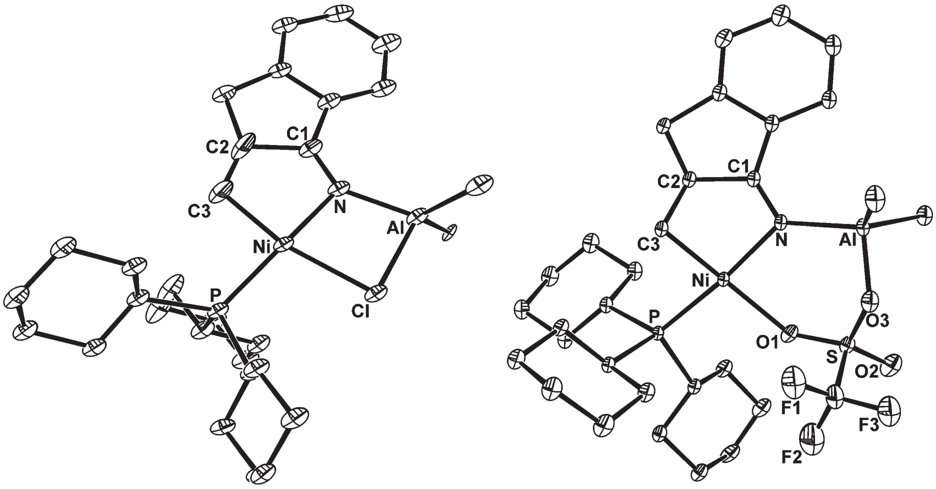
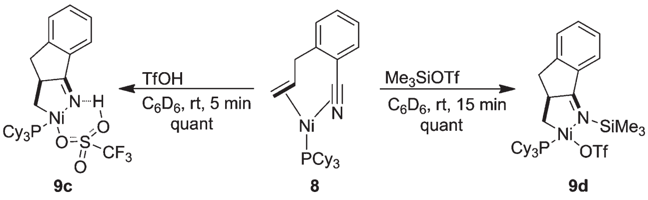


Figure 5. ORTEP drawings of **9a** (left) and **9b** (right) with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity.

Scheme 6. Oxidative Cyclization of 8 Promoted by ROTf (R = H and Me_3Si)



^{13}C NMR spectra were recorded at room temperature on JEOL GSX-270S, JEOL AL-400 and BRUKER DPX-400 spectrometers. The chemical shifts in ^1H and ^{13}C NMR spectra were recorded relative to Me_4Si ($\delta_H = \delta_C = 0$) or residual C_6D_5H (δ_H and δ_C = 7.16 and 128.0, respectively). The chemical shifts in ^{31}P NMR spectra were recorded using 85% H_3PO_4aq as an external standard. Assignment of the resonances observed in ^1H and ^{13}C NMR spectra was based on $^1H-^1H$ COSY, HMQC, and HMBC experiments. Elemental analyses were performed at Instrumental Analysis Center, Faculty of Engineering, Osaka University. X-ray crystal data were collected with a Rigaku RAXIS-RAPID Imaging Plate diffractometer. Crystallographic data are summarized in Table 1. Several nickel complexes containing aluminum atom as a component are too sensitive toward oxygen or moisture to obtain accurate elemental analysis.

Materials. The degassed and distilled solvents (benzene, 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.

Generation of *trans*-(P^nBu_3)$_2$Ni(C_6H_4-$CH_2C(CH_3){=}CH_2$)-($C{\equiv}N\cdot Al(CH_3)_2Cl$) (2). To a solution of $Ni(cod)_2$ (6.9 mg, 0.025 mmol) and P^nBu_3 (12.5 μL, 0.050 mmol) in 0.5 mL of C_6D_6 was added 2-(2-methylallyl)benzonitrile (**1**) (3.9 mg, 0.025 mmol) at room temperature. After 15 min, generation of Ni(cod)(P^nBu_3)$_2$ was observed and **1** remained intact. The color of the solution changed gradually from yellow to light yellow by addition of Me_2AlCl (1.08 M solution in hexane, 23.0 μL, 0.025 mmol) to the mixture. After 45 h, the title complex **2** was generated quantitatively.

*Isolation of **2**.* To a solution of $Ni(cod)_2$ (110 mg, 0.40 mmol) and P^nBu_3 (200 μL, 0.80 mmol) in 3.0 mL of toluene at room temperature was added **1** (62.8 mg, 0.40 mmol) and Me_2AlCl (1.08 M solution in hexane, 370 μL, 0.40 mmol). The reaction mixture was thermostatted at 60 °C for 1 h and the color of the solution changed gradually from yellow to light yellow. All volatiles were removed *in vacuo* to give yellow oil (283 mg, 99%). The attempt to purify the crude product by recrystallization failed due to its high solubility. ^1H NMR (400 MHz, C_6D_6): δ −0.25 (s, 6H, -AlMe_2), 0.70−1.60 (m, 54H, P^nBu_3), 1.78 (s, 3H, $CH_2{=}C(CH_3)$-), 3.57 (s, 2H, -$C_6H_4CH_2$-), 4.87 (s, 1H, $CHH{=}C(CH_3)$-), 4.94 (s, 1H, $CHH{=}C(CH_3)$-), 6.80−7.13 (m, 4H, -C_6H_4-). $^{31}P\{^1H\}$ NMR (109 Hz, C_6D_6): δ 13.2 (s). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ −6.8 (s, -AlMe_2), 14.0 (s, P^nBu_3), 23.8 (d, J_{CP} = 6.0 Hz, P^nBu_3), 23.9 (s, $CH_2{=}C(CH_3)$-), 24.0 (d, J_{CP} = 14.0 Hz, P^nBu_3), 24.9 (d, J_{CP} = 6.0 Hz, P^nBu_3), 25.0 (d, J_{CP} = 6.0 Hz, P^nBu_3), 26.9 (s, P^nBu_3), 48.9 (s, -$C_6H_4CH_2$-), 113.1 (s, $CH_2{=}C(CH_3)$-), 123.2 (s, -C_6H_4-), 125.5 (s, -C_6H_4-), 128.5 (s, -C_6H_4-), 135.4 (t, J_{CP} = 4.0 Hz, -C_6H_4-), 143.4 (t, J_{CP} = 3.0 Hz, -C_6H_4-), 144.2 (s, $CH_2{=}C(CH_3)$-), 154.9 (t, J_{CP} = 24.5 Hz, -$C{\equiv}N$), 157.7 (t, J_{CP} = 27.5 Hz, -C_6H_4-).

Generation of (PCy_3)Ni(η^2:η^2-$CH_2{=}C(CH_3)CH_2C_6H_4C{\equiv}N$)-($PCy_3$) (3). To a solution of $Ni(cod)_2$ (6.9 mg, 0.025 mmol) and PCy_3 (7.0 mg, 0.025 mmol) in 0.5 mL of C_6D_6 was added **1** (4.1 mg, 0.026 mmol) at room temperature. The color of the solution immediately changed from orange to light yellow, resulting in the quantitative formation of **3**.

*Isolation of **3**.* To a toluene solution of $Ni(cod)_2$ (165.0 mg, 0.60 mmol) and PCy_3 (168.3 mg, 0.60 mmol) was added **1** (94.3 mg, 0.60 mmol) at room temperature. The color of the solution changed immediately from orange to light yellow. The reaction mixture was stirred for 15 min, and then all volatiles were removed *in vacuo* to give yellow solids. The solids were washed with hexane to give **3** (271 mg, 91% yield). Further purification was achieved by recrystallization from toluene/hexane at −35 °C. ^1H NMR (400 MHz, C_6D_6): δ 1.22−2.31 (m, 33H, Cy), 1.41 (obscured by Cy, 3H, $CH_2{=}C(CH_3)$-), 2.30 (obscured by Cy, 1H, $CHH{=}C(CH_3)$-), 2.58 (d, J = 9.6 Hz, 1H, $CHH{=}C(CH_3)$-), 2.79 (d, J = 15.6 Hz, 1H, -C_6H_4CHH-), 3.42 (dd, J = 10.2, 15.6 Hz, 1H, -C_6H_4CHH-), 6.94 (dd, J = 6.8, 6.8 Hz, 1H, -C_6H_4-), 7.05−7.11 (m, 2H, -C_6H_4-), 8.10 (d, J = 7.2 Hz, 1H, -C_6H_4-). $^{31}P\{^1H\}$ NMR (109 Hz, C_6D_6): δ 37.5 (s). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 21.9 (d, J_{CP} = 2.0 Hz, $CH_2{=}C(CH_3)$-), 26.1 (s, Cy), 27.2 (d, J_{CP} = 3.0 Hz, Cy), 27.3 (d, J_{CP} = 3.0 Hz, Cy), 29.8 (d, J_{CP} = 3.0 Hz, Cy), 33.7 (d, J_{CP} = 15.0 Hz, Cy), 41.9 (s, -$C_6H_4CH_2$-), 50.4 (d, J_{CP} = 4.0 Hz, $CH_2{=}C(CH_3)$-), 76.9 (d, J_{CP} = 11.0 Hz, $CH_2{=}C(CH_3)$-), 115.7 (s, -C_6H_4-), 126.6 (s, -C_6H_4-), 127.6 (s, -C_6H_4-), 129.6 (s, -C_6H_4-), 130.1 (s, -C_6H_4-), 147.1 (d, J_{CP} = 6.0 Hz, -C_6H_4-), 154.9 (d, J_{CP} = 8.0 Hz, -$C{\equiv}N$). Anal. Calcd for $C_{29}H_{44}NNiP$: C, 70.18; H, 8.94; N, 2.82. Found: C, 69.40; H, 8.69; N, 2.75.

*Reaction of **3** with $AlMe_2Cl$.* To a solution of **3** (9.9 mg, 0.02 mmol) in 0.5 mL of C_6D_6 was added Me_2AlCl (1.08 M solution in hexane, 19.0 μL,

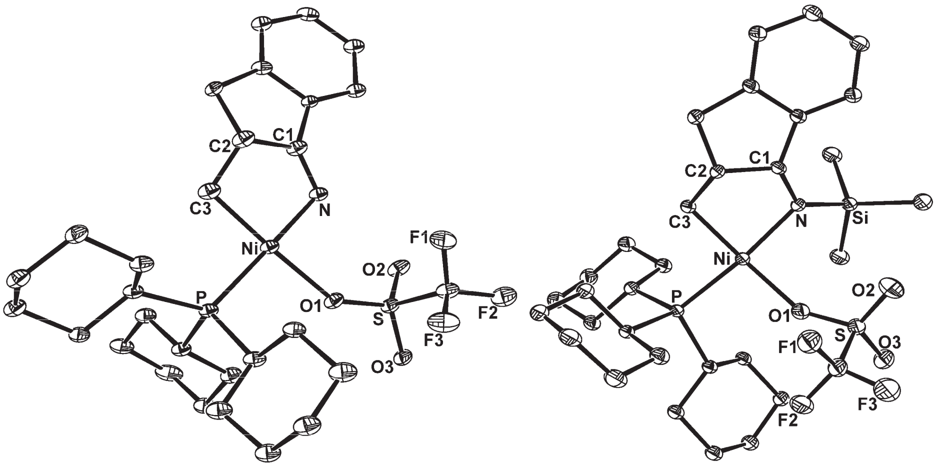
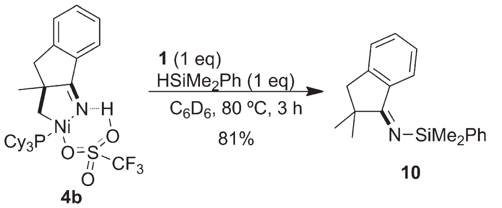


Figure 6. ORTEP drawings of **9c** (left) and **9d** (right) with thermal ellipsoids at the 30% probability level. H atoms and solvated molecules in **9d** (C_7H_8) are omitted for clarity.

Scheme 7. Reaction of 4b with HSiMe$_2$Ph in the Presence of 1

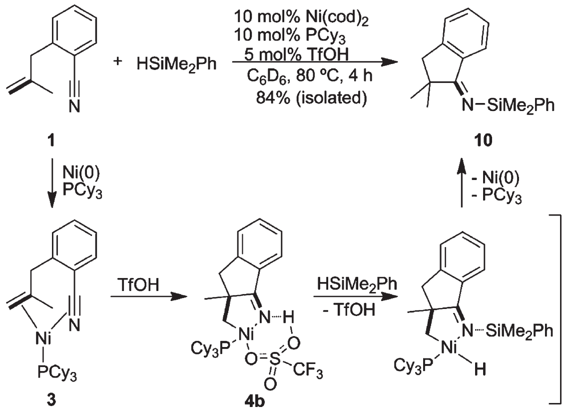


0.02 mmol) at room temperature. The color of the solution gradually changed from yellow to orange, resulting in the quantitative formation of a nickeladihydropyrrole (**4a**).

*Isolation of **4a**.* To a toluene solution of Ni(cod)$_2$ (110.0 mg, 0.40 mmol), PCy$_3$ (112.2 mg, 0.40 mmol) and **1** (62.8 mg, 0.40 mmol) was added Me$_2$AlCl (1.08 M solution in hexane, 370 μL, 0.40 mmol) at room temperature. The color of the solution changed from yellow to reddish orange. The reaction mixture was stirred for 2 h, and then all volatiles were removed *in vacuo* to give orange solids. The solids were washed with hexane to give **4a** (223 mg, 95%). Further purification was achieved by recrystallization from toluene/hexane at −35 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 0.04 (s, 3H, -Al*Me*$_2$), 0.13 (s, 3H, -Al*Me*$_2$), 0.81 (dd, *J* = 9.0, 9.0 Hz, 1H, -Ni-CH*H*-), 1.11−2.03 (m, 33H, Cy), 1.73 (obscured by Cy, 1H, -Ni-C*H*H-), 1.78 (obscured by Cy, 3H, -Ni-CH$_2$C(C*H*$_3$)-), 2.46 (d, *J* = 15.8 Hz, 1H, -C$_6$H$_4$CH*H*-), 2.55 (d, *J* = 15.8 Hz, 1H, -C$_6$H$_4$C*H*H-), 6.88 (d, *J* = 7.0 Hz, 1H, -C$_6$*H*$_4$-), 6.96 (dd, *J* = 6.2, 7.0 Hz, 1H, -C$_6$*H*$_4$-), 7.06 (dd, *J* = 6.2, 7.0 Hz, 1H, -C$_6$*H*$_4$-), 7.69 (d, *J* = 7.0 Hz, 1H, -C$_6$*H*$_4$-). ^{31}P{^{1}H} NMR (109 MHz, C$_6$D$_6$): δ 26.7 (s). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ −7.2 (s, -Al*Me*$_2$), −5.9 (s, -Al*Me*$_2$), 24.0 (d, J_{CP} = 26.0 Hz, -NiCH$_2$-), 26.9 (s, Cy), 28.0 (s, Cy), 28.1 (s, Cy), 30.3 (d, J_{CP} = 12.0 Hz, Cy), 32.1 (s, -NiCH$_2$C(CH$_3$)-), 33.9 (d, J_{CP} = 18.0 Hz, Cy), 40.5 (s, -C$_6$H$_4$CH$_2$-), 68.0 (d, J_{CP} = 8.0 Hz, -NiCH$_2$C(CH$_3$)-), 122.7 (s, -C$_6$H$_4$-), 127.5 (s, -C$_6$H$_4$-), 127.8 (s, -C$_6$H$_4$-), 131.5 (s, -C$_6$H$_4$-), 134.6 (s, -C$_6$H$_4$-), 154.5 (s, -C$_6$H$_4$-), 202.2 (s, -C═N(AlMe$_2$)Ni-). Anal. Calcd for C$_{31}$H$_{50}$AlClNNiP: C, 63.23; H, 8.56; N, 2.38. Found: C, 62.63; H, 8.40; N, 2.36.

*Reaction of **3** with TfOH.* To a solution of **3** (19.9 mg, 0.04 mmol) in 0.5 mL of C$_6$D$_6$ was added TfOH (3.5 μL, 0.04 mmol) at room temperature. The color of the solution immediately changed from yellow to light yellow, resulting in the quantitative formation of a nickeladihydropyrrole (**4b**).

Scheme 8. Ni(0)/PCy$_3$/TfOH-Catalyzed Reaction of 1 with HSiMe$_2$Ph



*Isolation of **4b**.* To a toluene solution of Ni(cod)$_2$ (137.5 mg, 0.50 mmol), PCy$_3$ (140.2 mg, 0.50 mmol) and **1** (87.5 mg, 0.56 mmol) was added TfOH (44 μL, 0.50 mmol) at room temperature. The color of the solution changed from yellow to reddish orange. The reaction mixture was stirred for 15 min, and then all volatiles were removed *in vacuo* to give yellow solids. The solids were washed with hexane to give **4b** (315 mg, 97%). Further purification was achieved by recrystallization from THF/hexane at −35 °C. ^{1}H NMR (400 MHz, THF-*d*$_8$): δ 0.59 (m, 1H, -Ni-CH*H*-), 1.20−2.20 (m, 33H, Cy), 1.33 (obscured by Cy, 1H,-Ni-C*H*H-), 1.72 (obscured by Cy, 3H, -NiCH$_2$C(C*H*$_3$)-), 2.72 (d, *J* = 16.2 Hz, 1H, -C$_6$H$_4$CH*H*-), 2.77 (d, *J* = 16.2 Hz, 1H, - C$_6$H$_4$C*H*H-), 7.29 (d, *J* = 7.6 Hz, 1H, -C$_6$H$_4$-), 7.34 (dd, *J* = 7.6, 7.6 Hz, 1H, -C$_6$H$_4$-), 7.49 (dd, *J* = 7.6, 7.6 Hz, 1H, -C$_6$H$_4$-), 7.62 (brs, 1H, -C$_6$H$_4$-), 8.95 (brs, 1H, -N*H*). ^{31}P{^{1}H} NMR (109 MHz, THF-*d*$_8$): δ 27.1 (s). ^{13}C{^{1}H} NMR (100 MHz, THF-*d*$_8$): δ 17.4 (brs, -NiCH$_2$-), 27.6 (s, Cy), 28.6 (s, Cy), 28.8 (s, Cy), 30.8 (d, J_{CP} = 9.2 Hz, Cy), 32.0 (brs, -NiCH$_2$C(CH$_3$)-), 33.1 (d, J_{CP} = 20.7 Hz, Cy), 41.7 (s, -C$_6$H$_4$CH$_2$-), 63.3 (s, -NiCH$_2$C(CH$_3$)-), 124.0 (brs, -C$_6$H$_4$-), 128.1 (s, -C$_6$H$_4$-), 128.7 (s, -C$_6$H$_4$-), 131.7 (d, J_{CP} = 9.2 Hz, -C$_6$H$_4$-), 155.1 (s, -C$_6$H$_4$-), 202.3 (s, -C═NH-Ni-). Anal. Calcd for C$_{30}$H$_{45}$F$_3$NNiO$_3$PS: C, 55.74; H, 7.02; N, 2.17. Found: C, 55.30; H, 7.09; N, 2.12.

*Reaction of 2-(3-Methyl-3-butenyl)benzonitrile (**5**) with Ni(cod)$_2$ in the Presence of PCy$_3$.* To a solution of Ni(cod)$_2$ (11.0 mg, 0.04 mmol) and PCy_3 (11.2 mg, 0.04 mmol) in 0.5 mL of C_6D_6 was added **5** (6.8 mg, 0.04 mmol) at room temperature. Monitoring of the reaction by means of NMR spectroscopy revealed that the conversion of the starting materials ($Ni(cod)_2$ and **5**) is 44% for 10 min and that generation of a mixture of η^2:η^2-6-ene-nitrile nickel(0) complex (**A**) and η^2-nitrile nickel(0) complex (**B**) is found to be generated in 9 and 35% yield, respectively. The resulting reaction mixture was treated with an equimolar amount of Me_2AlCl (1.08 M solution in hexane, 38.0 μL, 0.041 mmol) to give a complicated mixture. After 5 h, the reaction mixture was exposed to air for the sake of decomposition of nickel species, and then GC-Mass analysis of the crude product clearly showed that all of **5** were consumed and 2-(1-methyl-2,3-dihydro-1*H*-inden-1-yl)acetonitrile (**6**) was formed as a solo product. These nickel(0) complexes **A** and **B** were tentatively identified based on the characteristic resonances observed in the ^{1}H and ^{31}P NMR spectra.

Selected spectral data for **A**: ^{1}H NMR (400 MHz, C_6D_6): δ 2.48 (m, 1H, $CHH{=}C(CH_3)$-), 2.66 (m, 1H, $CHH{=}C(CH_3)$-), 7.63 (d, *J* = 7.2 Hz, 1H, -C_6H_4-). ^{31}P{^{1}H} NMR (109 Hz, C_6D_6): δ 36.6 (s, 1P). Selected spectral data for **B**: ^{1}H NMR (400 MHz, C_6D_6): δ 1.80 (s, 3H, $CH_2{=}C(CH_3)$-), 2.56 (m, 2H, $CH_2{=}C(CH_3)CH_2CH_2$-), 3.02 (m, 2H, $CH_2{=}C(CH_3)CH_2CH_2$-), 4.88 (s, 1H, $CHH{=}C(CH_3)$-), 4.97 (s, 1H, $CHH{=}C(CH_3)$-), 7.42 (br s, 1H, -C_6H_4-). ^{31}P{^{1}H} NMR (109 Hz, C_6D_6): δ 33.0 (d, J_{PP} = 41.5 Hz, 1P), 47.9 (d, J_{PP} = 41.5 Hz, 1P).

Spectral data of **6** were identical to that previously reported.[14c]

Generation of (PCy_3)Ni(η^2:η^2-$CH_2{=}CHCH_2C_6H_4C{\equiv}N$) (8).

To a solution of $Ni(cod)_2$ (5.5 mg, 0.02 mmol) and PCy_3 (5.6 mg, 0.02 mmol) in 0.5 mL of C_6D_6 was added 2-allylbenzonitrile (**7**) (2.9 mg, 0.02 mmol) at room temperature. The color of the solution changed immediately from orange to yellow, resulting in the quantitative formation of **8**.

Isolation of ***8***. To a toluene solution of $Ni(cod)_2$ (328.9 mg, 1.20 mmol) and PCy_3 (336.8 mg, 1.20 mmol) was added **7** (172.0 mg, 1.20 mmol) at room temperature. The color of the solution changed immediately from orange to yellow. The reaction mixture was stirred for 15 min, and then all volatailes were removed *in vacuo* to give yellow solids. The solids were washed with hexane to give **8** (572 mg, 99% yield). Further purification was achieved by recrystallization from toluene/hexane at −20 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 1.14−2.33 (m, 33H, Cy), 2.30 (obscured by Cy, 1H, $CHH{=}CH$-), 2.49 (dd, *J* = 13.0, 14.4 Hz, 1H, -C_6H_4CHH-), 2.67 (dd, *J* = 8.4, 8.8 Hz, 1H, $CHH{=}CH$-), 3.31 (m, $CH_2{=}CH$-), 3.52 (dd, *J* = 13.0, 12.8 Hz, 1H, -C_6H_4CHH-), 6.93 (dd, *J* = 6.8, 6.8 Hz, 1H, -C_6H_4-), 7.04−7.06 (m, 2H, -C_6H_4-), 8.08 (d, *J* = 7.2 Hz, 1H, -C_6H_4-). ^{31}P{^{1}H} NMR (109 Hz, C_6D_6): δ 37.4 (s). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 27.0 (s, Cy), 28.1 (d, J_{CP} = 4.0 Hz, Cy), 28.2 (d, J_{CP} = 2.0 Hz, Cy), 30.7 (s, Cy), 34.8 (d, J_{CP} = 15.0 Hz, Cy), 37.1 (s, $CH_2{=}CHCH_2$-), 46.4 (d, J_{CP} = 4.0 Hz, $CH_2{=}CHCH_2$-), 69.6 (d, J_{CP} = 11.0 Hz, $CH_2{=}CHCH_2$-), 117.9 (s, -C_6H_4-), 127.7 (s, -C_6H_4-), 129.8 (s, -C_6H_4-), 130.6 (d, J_{CP} = 2.0 Hz, -C_6H_4-), 131.0 (s, -C_6H_4-), 148.8 (d, J_{CP} = 6.0 Hz, -C_6H_4-), 153.4 (d, J_{CP} = 6.0 Hz, -$C{\equiv}N$). Anal. Calcd for $C_{28}H_{42}NNiP$: C, 69.73; H, 8.78; N, 2.90. Found: C, 68.54; H, 8.75; N, 2.95.

Reaction of ***8*** *with* $AlMe_2Cl$. To a solution of **8** (9.6 mg, 0.02 mmol) in 0.5 mL of C_6D_6 was added Me_2AlCl (1.04 M solution in hexane, 19.0 μL, 0.02 mmol) at room temperature. The color of the solution changed immediately from yellow to reddish orange to give a nickeladihydropyrrole (**9a**) in quantitative yield.

Isolation of ***9a***. To a toluene solution of **8** (96.5 mg, 0.20 mmol) was added Me_2AlCl (1.04 M solution in hexane, 190 μL, 0.20 mmol) at room temperature. The color of the solution changed from yellow to reddish orange. The reaction mixture was stirred for 10 min, and then all volatiles were removed *in vacuo* to give reddish orange solids. The solids were washed with hexane to give **9a** (110 mg, 96%). Further purification was achieved by recrystallization from toluene/hexane at −20 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 0.06 (s, 3H, -$AlMe_2$), 0.11 (s, 3H, -$AlMe_2$), 0.92 (dd, *J* = 8.0, 16.8 Hz, 1H, -Ni-CHH-), 1.08−2.00 (m, 33H, Cy), 1.60 (obscured by Cy, 1H, -Ni-CHH-), 2.23 (dd, *J* = 8.0, 16.0 Hz, 1H, -C_6H_4CHH-), 2.60 (dd, *J* = 6.4, 16.0 Hz, 1H, -C_6H_4CHH-), 3.49 (m, 1H, -$NiCH_2CH$-), 6.83 (d, *J* = 7.6 Hz, 1H, -C_6H_4-), 6.95 (dd, *J* = 7.0, 7.6 Hz, 1H, -C_6H_4-), 7.03 (dd, *J* = 7.0, 7.6 Hz, 1H, -C_6H_4-), 7.66 (d, *J* = 7.6 Hz, 1H, -C_6H_4-). ^{31}P{^{1}H} NMR (109 MHz, C_6D_6): δ 26.8 (s). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ −7.1 (s, -$AlMe_2$), −5.8 (s, -$AlMe_2$), 15.2 (d, J_{CP} = 27.0 Hz, -$NiCH_2$-), 26.8 (s, Cy), 27.9 (d, J_{CP} = 3.0 Hz, Cy), 28.0 (d, J_{CP} = 3.0 Hz, Cy), 30.3 (d, J_{cp} = 27.0 Hz, Cy), 33.1 (s, -$NiCH_2CHCH_2$-), 33.2 (d, J_{cp} = 19.0 Hz, Cy), 64.1 (d, J_{CP} = 8.0 Hz, -$NiCH_2CH$-), 122.0 (s, -C_6H_4-), 127.1 (s, -C_6H_4-), 128.6 (s, -C_6H_4-), 131.4 (s, -C_6H_4-), 135.6 (s, -C_6H_4-), 155.8 (s, -C_6H_4-), 198.6 (s, -$C{=}N(AlMe_2)Ni$-). Anal. Calcd for $C_{30}H_{48}AlClNNiP$: C, 62.69; H, 8.42; N, 2.44. Found: C, 61.99; H, 8.31; N, 2.34.

Reaction of ***8*** *with* Me_2AlOTf. To a solution of **8** (19.3 mg, 0.04 mmol) in 0.5 mL of C_6D_6 was added Me_2AlOTf (THF adduct, 10.0 μL, 0.04 mmol) at room temperature. The color of the solution changed immediately from yellow to reddish orange to give a nickeladihydropyrrole (**9b**) in quantitative yield.

Isolation of ***9b***. To a toluene solution of **8** (289.2 mg, 0.60 mmol) was added Me_2AlOTf (THF adduct, 150 μL, 0.60 mmol) at room temperature. The color of the solution changed from yellow to red. The reaction mixture was stirred for 15 min, and then all volatiles were removed *in vacuo* to give dark orange solids. The solids were washed with hexane to give **9b** as yellow microcrystalline (355 mg, 86%). Further purification was achieved by recrystallization from toluene/hexane at −20 °C. ^{1}H NMR (400 MHz, C_6D_6): δ −0.05 (s, 3H, -$AlMe_2$), −0.01 (s, 3H, -$AlMe_2$), 0.43 (m, 1H, -Ni-CHH-), 1.00−2.00 (m, 33H, Cy), 1.10 (obscured by Cy, 1H, -Ni-CHH-), 2.19 (dd, *J* = 6.4, 16.0 Hz, 1H, -C_6H_4CHH-), 2.57 (dd, *J* = 8.6, 16.0 Hz, 1H, -C_6H_4CHH-), 3.49 (m, 1H, -$NiCH_2CH$-), 6.82 (d, *J* = 6.8 Hz, 1H, -C_6H_4-), 6.97 (dd, *J* = 7.4, 7.6 Hz, 1H, -C_6H_4-), 7.02 (dd, *J* = 6.8, 7.4 Hz, 1H, -C_6H_4-), 8.04 (d, *J* = 7.6 Hz, 1H, -C_6H_4-). ^{31}P{^{1}H} NMR (109 MHz, C_6D_6): δ 24.7 (s). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ −8.4 (s, -$AlMe_2$), −6.6 (s, -$AlMe_2$), 10.4 (d, J_{CP} = 32.0 Hz, -$NiCH_2$-), 26.8 (s, Cy), 27.9 (d, J_{CP} = 9.0 Hz, Cy), 28.0 (d, J_{CP} = 9.0 Hz, Cy), 30.0 (s, Cy), 30.3 (s, Cy), 33.0 (d, J_{cp} = 19.0 Hz, Cy), 33.4 (d, J_{CP} = 5.0 Hz, -$NiCH_2CHCH_2$-), 63.8 (d, J_{CP} = 6.0 Hz, -$NiCH_2CH$-), 124.9 (s, -C_6H_4-), 126.9 (s, -C_6H_4-), 127.0 (s, -C_6H_4-), 131.6 (s, -C_6H_4-), 135.6 (d, J_{CP} = 4.0 Hz, -C_6H_4-), 155.1 (s, -C_6H_4-), 199.5 (d, J_{CP} = 5.0 Hz, -$C{=}N(AlMe_2OTf)Ni$-). Anal. Calcd for $C_{31}H_{48}AlF_3NNiO_3PS$: C, 54.08; H, 7.03; N, 2.03. Found: C, 51.51; H, 6.93; N, 2.17.

Reaction of ***8*** *with TfOH*. To a solution of **8** (9.6 mg, 0.02 mmol) in 0.5 mL of C_6D_6 was added TfOH (1.8 μL, 0.02 mmol) at room temperature. The color of the solution immediately changed from yellow to orange, resulting in the quantitative formation of a nickeladihydropyrrole (**9c**).

Isolation of ***9c***. To a toluene solution of **8** (241.2 mg, 0.50 mmol) was added TfOH (44.0 μL, 0.50 mmol) at room temperature. The color of the solution changed from orange to dark red. The reaction mixture was stirred for 20 min, and then insoluble was filtered to remove by passing through a pad of Celite. The filtrate was concentrated *in vacuo* to give yellow solids. The solids were washed with hexane to give **9c** (306 mg, 97%). Further purification was achieved by recrystallization from THF/hexane at −20 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 0.44 (dd, *J* = 8.8, 17.6 Hz, 1H, -Ni-CHH-), 0.87 (dd, *J* = 8.8, 8.8 Hz, 1H, -Ni-CHH-), 1.10−2.10 (m, 33H, Cy), 1.95 (obscured by Cy, 1H, -C_6H_4CHH-), 2.42 (dd, *J* = 8.4, 16.0 Hz, 1H, -C_6H_4CHH-), 2.98 (m, 1H, -$NiCH_2CH$-), 6.67 (d, *J* = 7.6 Hz, 1H, -C_6H_4-), 6.73 (dd, *J* = 7.6, 7.6 Hz, 1H, -C_6H_4-), 6.81 (d, *J* = 7.6 Hz, 1H, -C_6H_4-), 6.94 (dd, *J* = 7.6, 7.6 Hz, 1H, -C_6H_4-), 9.13 (brs, 1H, -N*H*). ^{31}P{^{1}H} NMR (109 MHz, C_6D_6): δ 27.2 (s). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 17.4 (d, J_{cp} = 32.0 Hz, -$NiCH_2$-), 26.6 (s, Cy), 27.6 (d, J_{cp} = 5.0 Hz, Cy), 27.7 (d, J_{cp} = 5.0 Hz, Cy), 29.7 (s, Cy), 30.0 (s, Cy), 32.2 (d, J_{cp} = 20.0 Hz, Cy), 33.0 (d, J_{CP} = 5.0 Hz, -$NiCH_2CHCH_2$-),57.4 (d, J_{CP} = 5.0 Hz, -$NiCH_2CH$-),122.5 (s, -C_6H_4-), 126.2 (s, -C_6H_4-), 128.2 (s, -C_6H_4-), 131.7 (s, -C_6H_4-), 132.5 (s, -C_6H_4-), 154.5 (s, -C_6H_4-), 197.4 (s, -CNHNi-). Anal. Calcd for $C_{29}H_{43}F_3NNiO_3PS$: C, 55.08; H, 6.85; N, 2.21. Found: C, 55.31; H, 6.91; N, 2.27.

Reaction of ***8*** *with TMSOTf.* To a solution of **8** (9.6 mg, 0.02 mmol) in 0.5 mL of C_6D_6 was added TMSOTf (3.6 μL, 0.02 mmol) at room temperature. The color of the solution immediately changed from yellow to orange, resulting in the quantitative formation of a nickeladihydropyrrole (**9d**).

Isolation of ***9d***. To a toluene solution of **8** (192.9 mg, 0.40 mmol) was added TMSOTf (72.0 μL, 0.40 mmol) at room temperature. The color of the solution changed from yellow to red. The reaction mixture was stirred for 15 min, and then all volatiles were removed *in vacuo* to give vermillion solids. The solids were washed with hexane to give **9d** (278 mg, 99%). Further purification was achieved by recrystallization from toluene/hexane at −20 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 0.34 (dd, J = 8.4, 11.2 Hz, 1H, -Ni-CH*H*-), 0.69 (s, 9H, -TMS), 0.83 (m, 1H, -Ni-C*H*H-), 1.20−2.40 (m, 33H, Cy), 2.05 (obscured by Cy, 1H, -C_6H_4CH*H*-), 2.49 (dd, J = 8.4, 16.4 Hz, 1H, -C_6H_4C*H*H-), 4.21 (m, 1H, -NiCH$_2$C*H*-), 6.76 (d, J = 7.8 Hz, 1H, -C_6H_4-), 6.84 (dd, J = 7.6, 7.8 Hz, 1H, -C_6H_4-), 7.00 (dd, J = 7.6, 7.8 Hz, 1H, -C_6H_4-), 7.54 (d, J = 7.8 Hz, 1H, -C_6H_4-). ^{31}P{^{1}H} NMR (109 MHz, C_6D_6): δ 24.5 (s). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 2.20 (s, -TMS), 9.9 (d, J_{cp} = 33.0 Hz, -NiCH$_2$-), 27.0 (s, Cy), 28.1 (m, Cy), 30.6 (s, Cy), 33.8 (d, J_{cp} = 19.0 Hz, Cy), 34.3 (s, -C_6H_4C*H*$_2$-), 61.2 (s, -NiCH$_2$CH-), 126.2 (s, -C_6H_4-), 127.0 (s, -C_6H_4-), 127.9 (s, -C_6H_4-), 132.9 (s, -C_6H_4-), 133.7 (s, -C_6H_4-), 156.2 (s, -C_6H_4-), 199.9 (s, -CN(TMS)Ni-). Anal. Calcd for $C_{32}H_{51}F_3NNiO_3PSSi$: C, 54.55; H, 7.30; N, 1.99. Found: C, 55.00; H, 7.33; N, 2.10.

Reaction of ***4b*** *with HSiMe$_2$Ph in the Presence of* ***1***. A solution of **4b** (38.8 mg, 0.06 mmol), HSiMe$_2$Ph (9.2 μL, 0.06 mmol) and **1** (9.4 mg, 0.06 mmol) in 0.5 mL of C_6D_6 was heated at 80 °C for 3 h. The yellow suspension changed to a red solution along with precipitation of a little amount of Ni black. Monitoring the reaction by means of ^{1}H NMR revealed that HSiMe$_2$Ph and **1** were fully consumed after 3 h. Then, all volatiles were removed *in vacuo* to give yellow solids. Extraction with hexane followed by concentration under N_2 atmosphere gave a silanamine (**10**) in 81% yield.

Catalytic Reaction of HSiMe$_2$Ph with ***1*** *in the Presence of TfOH.* To a solution of Ni(cod)$_2$ (5.5 mg, 0.02 mmol) and PCy$_3$ (5.6 mg, 0.02 mmol) in 0.5 mL of C_6D_6 was added **1** (31.4 mg, 0.20 mmol), TfOH (0.9 μL, 0.01 mmol) and HSiMe$_2$Ph (31.0 μL, 0.20 mmol) sequentially. The solution was heated at 80 °C for 4 h. The color of the solution changed from yellow to red with a small amount of Ni black. All volatiles were removed *in vacuo* to give yellow solids. Extraction with hexane followed by concentration under N_2 atmosphere gave **10** (48 mg, 84%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.65 (s, 6H, -Si*Me*$_2$Ph), 1.13 (s, 6H, (C*H*$_3$)$_2$C-), 2.65 (s, 2H, -C_6H_4C*H*$_2$-), 6.96 (dd, J = 7.4, 7.4 Hz, 1H, -C_6H_4-), 7.05 (d, J = 7.6 Hz, 1H, -C_6H_4-), 7.10−7.28 (m, 1H of -C_6H_4- and 3H of -*Ph*), 7.63 (d, J = 7.6 Hz, 1H, -C_6H_4-), 7.82 (d, J = 6.8 Hz, 2H, -*Ph*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 1.4 (s, -Si*Me*$_2$Ph), 27.3 (s, (CH$_3$)$_2$C-), 44.3 (s, -C_6H_4CH$_2$-), 46.3 (s, (CH$_3$)$_2$C-), 124.8 (s, -C_6H_4-), 126.6 (s, -C_6H_4-), 127.1 (s, -C_6H_4-), 128.0 (s, *m*-Ph), 129.3 (s, *p*-Ph), 132.1 (s, -C_6H_4-), 134.0 (s, *o*-Ph), 138.5 (s, -C_6H_4-), 141.0 (s, *ipso*-Ph), 150.2 (s, -C_6H_4-), 187.3 (s, -CN-). HRMS Calcd for $C_{19}H_{23}NSi$ 293.1600, Found *m*/*z* 293.1595.

■ ASSOCIATED CONTENT

S Supporting Information. Crystallographic data (CIF) for **3**, **4a**−**b**, **8**, and **9a**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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