An Unsaturated Nickel(0) NHC Catalyst: Facile Preparation and Structure of Ni(0)(NHC)$_2$, Featuring a Reduction Process from Ni(II)(NHC)(acac)$_2$

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A facile synthetic route to Ni(0)(NHC)$_2$ from stable Ni(II)(acac)$_2$ was established without common but labile Ni(0) precursors. The intermediate is a divalent mono-NHC adduct of Ni(acac)$_2$, Ni(NHC)(acac)$_2$. Reduction of Ni(NHC)(acac)$_2$ in both the presence and absence of an NHC ligand gave Ni(NHC)$_2$ in ca. 90% and 40% conversions, respectively. Ni(NHC)$_2$, especially with bis(2,6-diisopropylphenyl)imidazolin-2-ylidene, has strong Ni−C(carbene) bonds and remarkable anagostic Ni−H(methyl) interactions, stabilizing its 14e unsaturated structure.

Introduction

Zerovalent-nickel-catalyzed organic reactions are now widely developed and quite important in organic synthesis, similar to the corresponding palladium chemistry.[1] In many cases, the addition of an appropriate ligand to Ni(COD)$_2$ or another nickel(0) precursor was the approach applied to generate a catalytically active species.[1] Otherwise, divalent nickel complexes, such as nickel acetylacetonate, acetate, and halides, which were used with ligands, were reduced to zerovalent active species in situ.[1] In each reaction, the catalyst activity is estimated by varying the ratio of the loading ligand to achieve the reaction efficiently. So it is always desired by organic synthetic chemists to know the structure of the active catalyst and its generated amount in situ. Further, in order to understand the catalytic mechanism precisely, using defined metal complexes close to the active species is required. However, the active catalysts have not been isolated in many reactions using zerovalent or divalent nickel precursors. Difficulties in the synthesis of these zerovalent nickel compounds may be one of the significant reasons, because nickel(0) precursors are sometimes toxic and less stable in air than stable palladium(0) compounds, such as Pd$_2$(dba)$_3$ and Pd(PPh$_3$)$_4$.

Recently, N-heterocyclic-carbene (NHC) ligands were frequently added as ligands coordinating to metals in the reaction media.[2] These carbenes can bind to metals more strongly than widely used phosphines to stabilize the active species. Our previous studies on the development of active and easy-to-prepare nickel(II) catalyst precursors bearing a bulky NHC ligand also demonstrated their usefulness in the well-known catalytic cross-coupling reactions.[3] Any zerovalent nickel NHC complexes, which were prepared from air-unstable Ni(COD)$_2$ and applied to catalytic reactions,[4] were not widely used by chemists probably because of their difficult preparation techniques using unstable Ni(0) precursors. This prompted us to introduce a simple plan, easily synthesized active nickel(0) NHC complexes by the reduction of stable nickel(II) NHC complexes in the last step without employing nickel(0) precursors, which, we thought, may solve the technical difficulties in preparation as much as possible. In the early days, some zerovalent nickel phosphine complexes were similarly synthesized directly from nickel(II) precursors.[5] Quite recently, Danopoulos and Pugh reported the synthesis of Ni(NHC)$_2$ from Ni(tmed)(CH$_3$)$_2$ with NHC.[6] Although Fort et al. developed a similar in situ method, mixing commercially available Ni(acac)$_2$ and NHC, with the subsequent addition of a reducing agent before adding substrates, neither were the nickel(0) NHC species isolated nor were the structures and the amount of the active catalyst known.[7]

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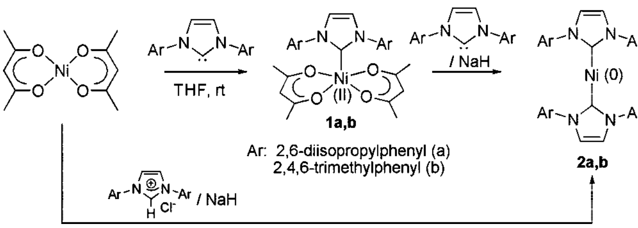
Scheme 1



Results and Discussion

Preparation of Ni(NHC)(acac)$_2$. In the process of establishing an easy preparative method for nickel(0) NHC complexes, first we synthesized Ni(acac)$_2$ complexes bearing NHC ligands and then reduced them, according to Fort's study. Although Nolan et al. showed the preparation of Pd(NHC)(acac)$_2$ by the reaction of Pd(acac)$_2$ with NHC,[8] to our surprise, a corresponding nickel compound has not been synthesized until now. The synthetic method of the NHC adduct was quite simple and is similar to Nolan's method; 1 equiv of the imidazolium chlorides and NaO^{t}Bu were added to the THF solution of Ni(acac)$_2$ at room temperature for about 2 h, forming complexes Ni(NHC)(acac)$_2$ (**1a** (NHC: bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) and **1b** (NHC: bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene)), which were purified by washing the reaction mixture with hexane, giving pale green needles in good yields (**1a**: 83%, **1b**: 65%) as shown in Scheme 1. Though preparation of the triphenylphosphine analogue required the addition of Et$_2$AlCl,[9] synthesis of complexes **1a**,**b** does not require such additives. Compounds **1a**,**b** are stable in air and do not regenerate Ni(acac)$_2$ and NHC in solutions at room temperature, so that the existence of Ni(acac)$_2$ was not detected by the ^{1}H NMR measurement of the reaction mixture in benzene-d_6. Using carbene instead of imidazolium chloride and a base also gave **1** in higher yields (in the case of **1a**: 88%). Even when more than 2 carbene equivalents to nickel were added to Ni(acac)$_2$, only **1a**,**b** were formed, in contrast to the formation of six-coordinated octahedral phosphine or pyridine adducts.[10] As Nolan et al. showed with the preparation of Pd(NHC)(acac)Cl by the reaction of Pd(acac)$_2$ with imidazolium chlorides,[11] we also mixed Ni(acac)$_2$ and imidazolium chloride and heated a 1,4-dioxane solution of the mixture at 100 °C for 24 h, but obtained only the starting materials.

Reduction of Ni(IPr)(acac)$_2$ (1a). The reduction of compound **1a** to obtain a zerovalent nickel species was tried with reducing agents, such as NaH, Na, *n*-BuLi, and NaO^{t}Bu, as shown in Table 1. The reduction of **1a** with NaH successfully gave a zerovalent nickel complex bearing two NHC ligands, Ni(IPr)$_2$ (**2a**), in 45% isolated yield, as deep purple crystals after recrystallization from a hexane solution at −30 °C (Table 1, entry 2). The reduction at around 70−80 °C gave only ca. 30% formation of **2a** after 24 h even in the presence of an excess amount of NaH (entry 1), whereas at 100 °C in 1,4-dioxane, more than 80% conversion resulting in the formation of **2a** was detected after 12 h (entry 2). After 18 h under the same conditions, the amount of compound **2a** was found to have increased to ca. 90% (entry 3). The observable products after hexane extraction were only **2a** and free carbene in the ^{1}H NMR spectra, and isolation of **2a** was successful by recrystallization only when the ratio of free carbene in the mixture was low enough, avoiding simultaneous crystallization of these compounds. Interestingly, the reduction of **1a** by NaH without adding NHC also gave only **2a**, which was detected in the ^{1}H NMR spectrum of the crude mixture (43% conversion of **1a** to **2a**) (Table 1, entry 4), suggesting that, in many catalytic reactions with Ni and NHC, in situ-generated nickel(0) species may have two NHC ligands as a stable form. In addition, the signals due to free carbene observed in the ^{1}H NMR spectrum of the crude mixture suggested that, in this reduction process, an NHC ligand is eliminated from some of the nickel(II) or nickel(0) species in some reaction steps and then free NHC binds to the reduced nickel(0) NHC species to form **2**. The resultant nickel species without an NHC ligand may not be the starting material, Ni(acac)$_2$, which could not be observed in the crude ^{1}H NMR spectra. We assumed that the nickel species might be converted to an ionic sodium salt, such as NaNi(acac)$_3$,[12] or some hydride complexes; however, the result of the ICP-MS spectrum using a water-extracted solution (containing HNO$_3$) showed that the nickel ion could not be detected at a known level. Other reduction using Na and a small amount of benzophenone also gave **2a** even at room temperature in lower yield (37% NMR yield) than that with NaH (Table 1 entry 5). After a reduction with 3 equiv of *n*-BuLi at room temperature, in the ^{1}H NMR spectrum of the crude mixture we found many products, including **2a** and free carbene, which were difficult to isolate from the mixture (entry 6). On the other hand, the addition of 3 equiv of NaO^{t}Bu or 1 equiv of *n*-BuLi did not give **2a** at all (entries 8 and 7).

Table 1. Reduction of 1a with Some Reducing Agents

entry	reducing agent (equiv)	IPr HCl/equiv	temp/°C	time/h	yields/%[a] (%)[b]
1[c]	NaH[d]	1.0	80	24	34
2	NaH[d]	1.0	100	12	81 (45)
3	NaH[d]	1.0	100	18	90
4	NaH[d]	0	100	18	43[f]
5	Na[de]	1.0	r.t.	18	37
6	*n*-BuLi (3.0)	1.0	r.t.	0.25	—[g]
7	*n*-BuLi (1.0)	0	r.t.	0.25	0
8	NaO^{t}Bu (3.0)	1.0	100	18	0

[a] Determined from a combination of the mass of the mixture of **2a** and carbene and ^{1}H NMR integrated ratios of these NHC-methyne signals around 6 ppm. [b] Determined by recrystallization. [c] THF was used as a solvent instead of 1,4-dioxane. [d] Excess amounts of the reducing agents were used. [e] A small amount of benzophenone was added. [f] Yield calculation was based on the total amount of **1a**. [g] The products, including **2a**, were so complicated that the yield could not be determined.

The reduction of **1a** in the presence of phosphines and phosphites, such as P(o-Tol)$_3$, PCy$_3$, PPh$_3$, and P(OPh)$_3$, resulted in the formation of a major product, **2a**, IPr, and some minor diamagnetic unknown products, possibly phosphine/NHC mixed Ni(0) complexes, which unfortunately could not be isolated. Finally, direct synthesis of **2a** from Ni(acac)$_2$ and 2 equiv of imidazolium chloride in the presence of NaH was conducted, successfully yielding 53% of **2a** (NMR yield) (Scheme 1). The moderate-yield formation of **2a** indicates that some unexpected

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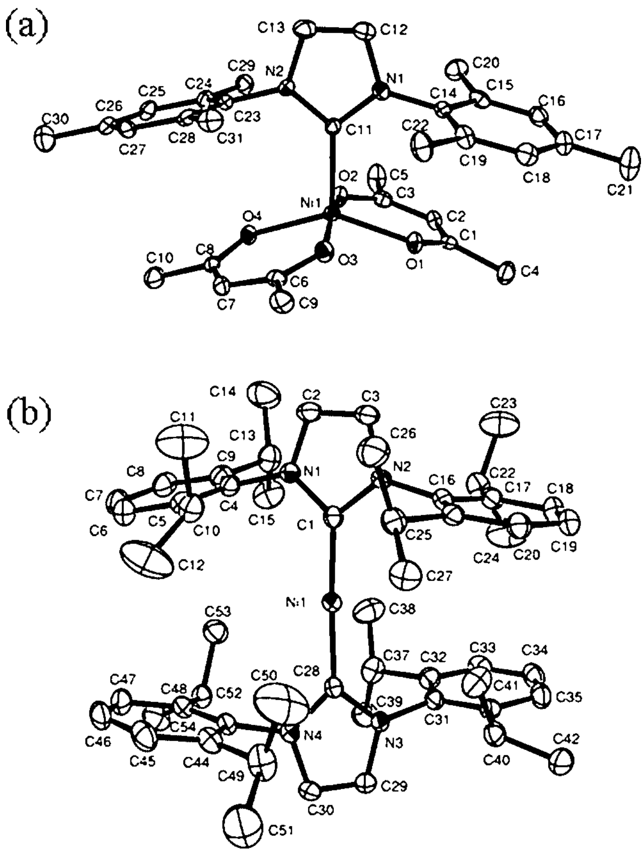

Figure 1. Crystal structures of (a) **1b** and (b) **2a** (30% probability thermal ellipsoids; all hydrogen atoms are omitted for clarity). Representative bond distances (Å) and angles (deg): **1b**: Ni(1)−C(11) 2.029(4); Ni(1)−O_{av} 2.017(3), C(11)−Ni(1)−O(1) 107.9(1), C(11)−Ni(1)−O(2) 94.8(1), C(11)−Ni(1)−O(4) 107.51(14), C(11)−Ni(1)−O(3) 98.3(1); **2a**: Ni(1)−C(1) 1.856(2), Ni(1)−C(28) 1.872(2), C(1)−Ni(1)−C(28) 177.78(10).

products of carbene or the Ni adduct are generated without isolating NHC or the NHC adduct of $Ni(acac)_2$.

Characterization of Ni(II) and Ni(0) Complexes. Isolated nickel(II) and nickel(0) NHC complexes, **1** and **2**, were identified by means of spectroscopic measurements and confirmed by X-ray crystallography. Compounds **1a** and **1b** were paramagnetic, and their ESR and magnetic susceptibility were measured. As shown in the Supporting Information, the $\chi_m T$ of both compounds were around 1 cm^3 K mol^{-1} from 5 to 300 K, suggesting that the spin quantum numbers, *S*, are 1 at the ground state. The ^1H NMR spectra also showed broad signals from −0.5 to 7.0 ppm. On the other hand, **2a** had already been synthesized from $Ni(COD)_2$, and the ^1H and ^{13}C resonances in C_6D_6 agree well with the reported data.[13]

The structures of **1a**, **1b**, and **2a** were determined by means of single-crystal X-ray diffraction studies. Unfortunately, due to a complex disorder in the crystal of **1a**, the structure could not be optimized at the final stage. As shown in Figure 1a, in contrast to its palladium analogue, having a 16-electron square-planer structure, complex **1b** has an 18-electron, five-coordinated, square-pyramidal structure around the nickel atom, which is well known in specific nickel(II) complexes.[14] The nickel−carbon(11) bond length (2.029(4) Å) was longer than previously reported nickel NHC complexes, $NiCl_2(IPr)_2$[3a] and NiCl(π-allyl)(1,3-di(*tert*-butyl)imidazolin-2-yl)[15] (1.933(6) and 1.926(2) Å, respectively), which have square-planar geometry. On the other hand, the structure of **2a** was similar to $Ni(IMes)_2$, which was determined by Arduengo et al.,[15] and the C−Ni−C angle was almost linear, 177.8(1)°. The nickel−carbon (NHC) bond lengths in **2a** were 1.856(2) and 1.872(2) Å, which are slightly longer than its mesityl analogue, $Ni(IMes)_2$ (1.827(6), 1.830(6) Å),[15] possibly due to the steric repulsion between two IPr ligands on both sides. In comparison with the Ni(II) halides $NiCl_2(IPr)_2$ (1.933(6) Å)[3a] and $NiCl_2$(1,3-biscyclohexylimidazolin-2-yl)$_2$ (1.911(2) Å),[16] they were 0.1 Å shorter. As pointed out in the DFT calculation of an analogous palladium(0) complex,[17] there might be two weak interactions between the unsaturated nickel atom and methyl protons of two isopropyl groups in one of two carbenes: the nickel−carbon (Ni(1)···C(41) and Ni(1)···C(53)) distances were 3.844 and 3.624 Å, which were obviously shorter than the other six Ni−C(methyl) lengths (4.2−5.2 Å). The Ni···H−C angles were 154.1° and 166.4°, suggesting not agostic but anagostic (largely electrostatic) interactions.[18] These interactions are probably flexible because of the appearance of only two equivalent signals in the ^1H NMR spectrum for **2a** due to 48 methyl protons at δ 1.09 and 1.23 in benzene-d_6. This prompted us to measure the IR spectrum for **2a** in the solid state in order to support the X-ray results. As a result of comparing it with that for free carbene, unfortunately, we could not find any visible absorption bands in the lower ν(CH) field that are assignable as C−H bonds longer than the normal C−H bonds. Agostic interaction of NHC with nickel was recently reported with $NiX_2(NHC)_2$ (NHC = 1,3-dialkylbenzimidazolin-2-ylidene).[19] However, rare examples of the demonstration of the agostic interaction in zerovalent nickel complexes are known; for example, a similar phenomenon leads to C−H activation at the aromatic ring in a carbene ligand by nickel(0) species,[20a] and an intermolecular version of an agostic interaction of a nickel(0) complex was reported previously.[20b]

DFT Calculations. While our previous reports showed that an NHC ligand exchange (ligand disproportionation) reaction did not occur even at 60 °C in the nickel(II) complex having IPr and triphenylphosphine ligands,[3a] this study indicated that the NHC-ligand migration easily occurred even at room temperature from the result of the above reduction processes. Although the carbene−metal bond strength of zerovalent palladium species is known to be weaker than its divalent analogues,[21] that of nickel(0) is unknown. Experimentally, we added more than 1 equiv of IMes to **2a** in THF at room temperature for more than 12 h, resulting in disproportionation of the carbenes to form $Ni(IMes)_2$ and IPr to some extent, suggesting that slow ligand exchange proceeded even at room temperature, possibly via an associative mechanism. So, the bond dissociation energies of the Ni(0) and Ni(II) complexes,

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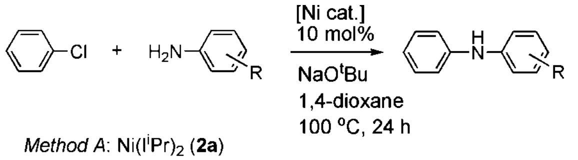
Table 2. Bond Dissociation Energies (BDE) of 2a and Ni(II) Complexes Predicted by the B3LYP/6-31G(d,p) Approach[a]

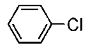
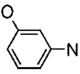
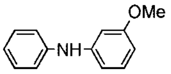
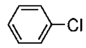
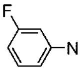
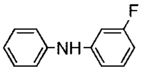
entry	complex	BDE/kcal mol^{-1}
1	**2a**	53
2	$NiCl_2(IPr)_2$	37
3	$NiCl_2(IPr)(PPh_3)$	47

[a] Bond dissociation energy was determined from the remainder of the zero-point energies of the ground state of IPr and the surplus nickel fragments calculated independently by DFT (B3LYP/6-31G(d, p)).

Table 3. Nickel-Catalyzed Amination of Chlorobenzene



Method A: $Ni(I^iPr)_2$ (**2a**)
Method B: $Ni(acac)_2$ + $[IPrH]^+Cl^-$ + NaH (Fort's results)

entry	aryl chloride	aniline	product	yield (%) *Method A*[a)]	yield (%) *Method B*[b)]
1				72	58
2				64	59

[a]Conditions in method A: **2a** (10 mol %), aniline (1.5 equiv of chlorobenzene), NaO^{t}Bu (1.8 equiv of chlorobenzene), in 1,4-dioxane, 100 °C, 24 h. Yields were determined by column chromatography (SiO_2). Yields of method B were cited from ref 22.

2a, $NiCl_2(IPr)_2$, and $NiCl_2(IPr)(PPh_3)$, were calculated on the basis of the DFT calculation (basis set: B3LYP/6-31G(d, p)).[22] They were estimated from the remainder of the zero-point energy of the ground state of IPr and the other nickel fragments calculated independently, and of $NiX_n(L)(IPr)$ ($n = 0$ or 2). As shown in Table 2, in sharp contrast to the palladium results in the literature,[21] the Ni(0)−C(carbene) bond dissociation was about 6−17 kcal mol^{-1} harder (53 kcal mol^{-1}) than the Ni(II)−C(carbene) bonds (36−47 kcal mol^{-1}), supporting the fact that $Ni(NHC)_2$ is stable enough at room temperature to hardly form a 12e monoadduct, [Ni(NHC)], in the ligand substitution.

Furthermore, from the calculation results, weak interactions of the nickel and two methyl hydrogen atoms in the same carbene can also be pointed out. The short distances between nickel and two methyl carbons of isopropyl groups, 3.187 and 3.384 Å (Ni···H: 2.098 and 2.296, C−H: 1.107 and 1.101 Å), were estimated and were shorter than the experimental results (Ni···C: 3.624 and 3.844 Å), as shown in the X-ray crystallography of **2a**. In contrast to the 14e bisphosphine complexes of palladium, which have no such interactions between metal and ligands,[23] these interactions could stabilize the coordinatively unsaturated nickel center of **2a**.

Catalytic amination of chlorobenzene with inactive anilines in the presence of **2a** was carried out (method A). Higher-yield formation of biarylamines from *m*-methoxyaniline and *m*-fluoroaniline (72% and 64%, respectively) (method A) in Table 3 was achieved in comparison with Fort's in situ Ni(0)-generation process (58% and 59%) (method B).[24] It is quite important that this result suggests that compound **2** is very close to the active catalyst species in these reactions.

Conclusion

In summary, a nickel(0) NHC complex, $Ni(NHC)_2$, which is close to the catalytically active species in the amination of aryl halides, for example, can be synthesized from the reduction of a new NHC adduct of nickel(II) acetylacetonate, $Ni(NHC)(acac)_2$, and was isolated and structurally determined. This synthetic method gave a 14e Ni(0) complex in high yield and was technically more facile than previous methods using air-unstable $Ni(COD)_2$ and NHC. The Ni(0) NHC complex easily exchanges carbene ligands, but from the DFT calculation results, formation of the 12e [Ni(0)NHC] species with the liberation of NHC hardly occurs in comparison with those of nickel(II) complexes. Catalytic applications of $Ni(NHC)(acac)_2$ and $Ni(NHC)_2$, exploration of the reduction routes from other divalent nickel complexes, and the synthesis of newly functionalized nickel(0) catalysts are now under way.

Experimental Section

General Comments. All experiments were carried out under an inert gas atmosphere using standard Schlenk techniques and a glovebox (MBraun UniLab) unless as otherwise noted. THF, 1,4-dioxane, hexane, and benzene-d_6 were distilled from benzophenone ketyl and stored under a nitrogen atmosphere. Chloroform-*d* was distilled from CaH and stored under a nitrogen atmosphere. Organic reagents used for coupling reactions were distilled just before use. Other reagents were used as received. Column chromatography of organic products was carried out using silica gel (Kanto Kagaku, silica gel 60N (spherical, neutral)). The ^1H NMR spectra were taken with a Varian Mercury Y plus 400 MHz spectrometer at room temperature. Chemical shifts (δ) were recorded in ppm from the solvent signal. IR spectra were recorded in cm^{-1} on a Perkin-Elmer Spectrum One spectrometer equipped with a universal diamond ATR. The ESR spectra were taken with a JEOL JES-RE1X ESR spectrometer at room temperature. The *g* value was calibrated with a standard Mn maker. The magnetic properties of the materials were investigated using a Quantum Design MPMS-5S superconducting quantum interference device magnetometer. ICP-MS spectra were taken with a Shimadzu ICPM-8500 spectrometer. The elemental analysis was carried out with a Yanaco CHN Corder MT-5, auto-sampler. The N-heterocyclic carbenes (IMes and I*i*Pr) were prepared according to the published methods.[25]

Synthesis of $Ni(NHC)(acac)_2$ (1a and 1b). In a typical example, bis(2,6-diisopropylphenyl)imidazolium chloride (468 mg, 1.10 mmol), NaO^{t}Bu (115 mg, 1.20 mmol), and THF (15 mL) were added to a 50 mL flask and stirred at room temperature for 30 min, followed by addition of $Ni(acac)_2$ (257 mg, 1.00 mmol) in THF (5 mL). After stirring for 2 h, the resulting suspension was filtered with Celite and evaporated. Wash with with hexane and drying under reduced pressure gave a pale green solid (536 mg, 83%) as **1a**. Anal. Calcd for $C_{37}H_{50}N_2O_4Ni$: C, 68.85; H, 7.81; N, 4.34. Found: C, 68.24; H, 7.63; N, 4.14. ^1H NMR (400 MHz, 20 °C, C_6D_6): δ 4.68, 3.98 (br), 0.76, −0.12 (br). IR (ν, cm^{-1}): 3182, 3073, 2963, 2870, 1585(vs), 1515(vs), 1404(vs), 1262, 1014, 922, 801, 757, 654, 569, 416.

Preparation of **1b** was carried out similarly with bis(2,4,6-trimethylphenyl)imidazolium chloride (188 mg, 0.55 mmol), NaO^{t}Bu

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(22) Calculation of the BDE of **1a** was also tried, but the square-pyramidal structure of **1a** was not stable at the calculation level (B3LYP 6-31G(d,p)).

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(58.0 mg, 0.60 mmol), and Ni(acac)$_2$ (129 mg, 0.50 mmol) to give a pale green solid (184 mg, 65%). Anal. Calcd for $C_{31}H_{38}N_2O_4Ni$: C, 66.33; H, 6.82; N, 4.99. Found: C, 66.08; H, 6.76; N, 5.05. ^{1}H NMR (400 MHz, 20 °C, C_6D_6): δ 6.80, 6.44, 5.59, 4.38 (br), 3.56, 2.87 (br), 1.32. IR (ν, cm^{-1}): 3170, 3069, 2962, 2919, 1583(vs), 1511(vs), 1397(vs), 1259, 1012, 920, 846, 757, 737, 693, 654, 568, 416.

Synthesis of Ni(NHC)$_2$ (2a) from 1a. The complex **1a** (129 mg, 0.20 mmol), bis(2,4,6-trimethylphenyl)imidazolium chloride (85.0 mg, 0.20 mmol), NaH (96.0 mg, 4.00 mmol), and 1,4-dioxane (15 mL) were added to a 50 mL flask and stirred at 100 °C for 12 h. After the volatile solvent was removed under reduced pressure, the residual solid was extracted with hexane. The resulting suspension was filtered through Celite and evaporated to give a deep purple crystalline solid containing **2a** and IPr carbene. Recrystallization from hexane at −30 °C afforded **2a** in 45% yield (74.7 mg). Anal. Calcd for $C_{54}H_{72}N_4Ni$: C, 77.59; H, 8.68; N, 6.70. Found: C, 77.30; H, 8.49; N, 6.69.

Synthesis of Ni(NHC)$_2$ (2a) from Ni(acac)$_2$. Direct synthesis of **2a** from nickel acetylacetonate is as follows: Ni(acac)$_2$ (26.0 mg, 0.100 mmol), bis(2,6-diisopropylphenyl)imidazolium chloride (84.7 mg, 0.200 mmol), NaH (48.0 mg, 2.00 mmol), and 1,4-dioxane (7.5 mL) were added to a 50 mL flask and stirred at 100 °C. Then the solvent was evaporated under reduced pressure. After the residual solid was extracted with hexane, filtration through Celite and subsequent evaporation of the solvent gave a dark purple solid (74.7 mg), which contained **2a** (0.077 mmol, 53%) and free carbene (0.053 mmol).

X-ray Diffraction Studies. Single crystals of **1b** (green needles) and **2a** (deep purple prisms) for X-ray diffraction studies were grown at −30 °C from toluene and hexane solutions, respectively. The data were collected at 123 K on a Rigaku Saturn CCD diffractometer with a confocal mirror using graphite-monochromated Mo Kα radiation (λ = 0.71070 Å). Data reductions of the measured reflections were carried out using the software package CrystalStructure (ver. 3.8). The structures were solved by direct methods (SIR2002)[26] and refined by full-matrix least-squares fitting based on F^2 using the program SHELXL 97-2 PC version.[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were located at ideal positions and were included in the refinement, but were restricted to ride on the atom to which they were bonded. Detailed data are shown in CIF files, available as Supporting Information.

DFT Calculations. DFT calculations were carried out with Gaussian 03 software at the Research Institute for Information Technology at Kyushu University. The B3LYP functional and 6-31G(d,p) basis set were used for the calculations. The initial structures of the nickel complexes were determined from the X-ray results: the coordinate data of the atoms were created from their CIF files with the software package Chem3D Pro 8.0. The fact that the obtained structures give no imaginary vibrational frequency shows that the obtained structures are energetically stable. The electron spin multiplicity of the compounds was set to be singlet in the calculations, which was determined from the result of the NMR measurements. Cartesian coordinates of the calculated compounds are available free as Supporting Information.

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Supporting Information Available: Detailed DFT calculation results, spectral data for the new compounds, **1a** and **1b**, Cartesian coordinates of the calculated compounds, and CIF data for **1b** and **2a** are available free of charge via the Internet at http://pubs.acs.org.

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