Supplementary Information for

"A New Aspect of Nickel-Catalyzed Grignard Cross-Coupling Reactions: Selective Synthesis, Structure, and Catalytic Behavior of a T-Shape Three-Coordinate Nickel(I) Chloride Bearing a Bullky NHC Ligand"

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S-1 Experimental

S-1-1 General

All experiments were carried out under an inert gas atmosphere using standard Schlenk techniques and glove box (MBraun UniLab) as otherwise noted. THF, toluene, hexane, benzene-d_6 were distilled from benzophenone ketyl and stored under a nitrogen atmosphere. Aryl halides 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 ^{1}H 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 *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 ESR spectra were taken with a JEOL RE-1X spectrometer equipped with ES-IPRITS DATA SYSTEM software on PC. The elemental analysis was carried out with YANACO CHN Corder MT-5, AUTO-SAMPLER. Gas Chromatography-Mass Spectrometry (GC-MS) was recorded in the mass range 1-1000 m/z on a JEOL JMS-GCmateII, using a little polar capillary column. The N-heterocyclic carbene (IPr) was prepared according to the published methods.[1] Synthesis of zerovalent nickel complex, $Ni(IPr)_2$ (**1**), was shown in our previous report.[2]

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[1] A. J. Arduengo III, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* 1992, **114**, 5530-5534.

[2] K. Matsubara, S. Miyazaki, Y. Koga, Y. Nibu, T. Hashimura, T. Matsumoto, *Organometallics*

S-1-2 Synthesis of NiCl(IPr)$_2$ (2) from Ni(IPr)$_2$ (1)

To the 20 mL Schlenk tube, Ni(IPr)$_2$ (167 mg, 0.20 mmol), 4-chlorotoluene (26.0 μL, 0.22 0mmol), and toluene (3.0 mL) were added at room temperature. After stirring the mixture for 5 h, the solvent was removed under reduced pressure. The residual solid was recrystallized from the hexane/THF (3/1) solution at -30 ^{o}C, yielding the crystals of **2** (60 mg, 34%). ^{1}H NMR (400 MHz, benzene-d_6) δ = -3.5, 2.8, 8.3, 8.7.

Other analyses including elemental analysis were unsuccessful unfortunately, because the compound was so unstable even in the solid state that rapid decomposition occurred in the air. Direct EI-MS measurement of **2** resulted in no appearance of the MS peaks. The purity of the compound was confirmed by ^{1}H NMR spectroscopy and X-ray diffraction studies using different crystals.

S-1-3 Synthesis of NiCl(IPr)$_2$ (2) from Ni(cod)$_2$

To the 20 mL Schlenk tube, Ni(cod)$_2$ (55 mg, 0.20 mmol) and THF (3.0 mL) were added. A solution of bis(2,6-diisopropylphenyl)imidazol-2-ylidene (159 mg, 0.410 mmol) in THF (3.0 mL) was slowly added with stirring at room temperature. After stirring the mixture for 5 h, the volatiles were removed under reduced pressure. Then, toluene (3 mL) and 4-chlorotoluene (26.0 μL, 0.22 0mmol) were added to the residual solid and dissolved at room temperature and the solution was stirred for 12 h. After removal of the solvent, the residual solid was recrystallized from the hexane/THF (3/1) solution at -30 ^{o}C, yielding the crystals of **2** (68 mg, 39%).

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S-1-4 Kumada-Corriu cross-coupling reactions using 2 as a catalyst

S-1-4-1 Cross-coupling reaction of 4-bromoanisole

The complex **2** (8.7 mg, 0.01 mmol), IPr (19.4 mg, 0.05 mmol), *p*-bromoanisole (125 μL, 1.0 mmol), and THF (1.0 mL) were added to the 20 mL Schlenk tube, and the mixture was stirred for five minutes at room temperature. Phenylmagnesium chloride (0.75 mL, 1.5 mmol, 2.0 M solution in THF) was added to the solution and stirred for 18 h at room temperature. Then, after the reaction was quenched by adding water (20 mL), the mixture was extracted with dichloromethane (20 mL × 4) and dried with magnesium sulfoxide. After removal of the solid, the solvent was evaporated and the yellow residual mixture was separated by column chromatography by eluting with 20% dichloromethane in hexane to give 4-methoxybiphenyl (171 mg, 93% yield).

4-Methoxybiphenyl (CAS: 613-37-6): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.54$ (t, $J = 8.0$ Hz, 4 H, PhH), 7.42 (t, $J = 8.0$ Hz, 2 H, PhH), 7.30 (t, $J = 8.0$ Hz, 1 H, PhH), 6.98 (d, $J = 8.0$ Hz, 2 H, PhH), 3.86 (s, 3 H, OCH_3).

S-1-4-2 Cross-coupling reaction of 4-bromobiphenyl

The complex **2** (8.7 mg, 0.01 mmol), IPr (19.4 mg, 0.05 mmol), 4-bromobiphenyl (233.1 mg, 1.00 mmol), and THF (1.0 mL) were added to the 20 mL Schlenk tube, and the mixture was stirred for five minutes at room temperature. Phenylmagnesium chloride (0.75 mL, 1.5 mmol, 2.0 M solution in THF) was added to the solution and stirred for 18 h at room temperature. Then, after the reaction was quenched by adding water (20 mL), the mixture was extracted with dichloromethane (20 mL × 4) and dried with magnesium sulfoxide. After removal of the solid, the solvent was evaporated and the yellow residual mixture was separated by column chromatography by eluting with hexane to give *p*-terphenyl (204.3 mg, 89% yield).

p-Terphenyl (CAS: 92-94-4): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (s, 4H, PhH), 7.65 (d, *J* = 7.2 Hz, 4H, PhH), 7.47 (t, *J* = 8.0 Hz, 4 H, PhH), 7.36 (t, *J* = 8.0 Hz, 2 H, PhH).

S-2 ^{1}H NMR spectra for 2

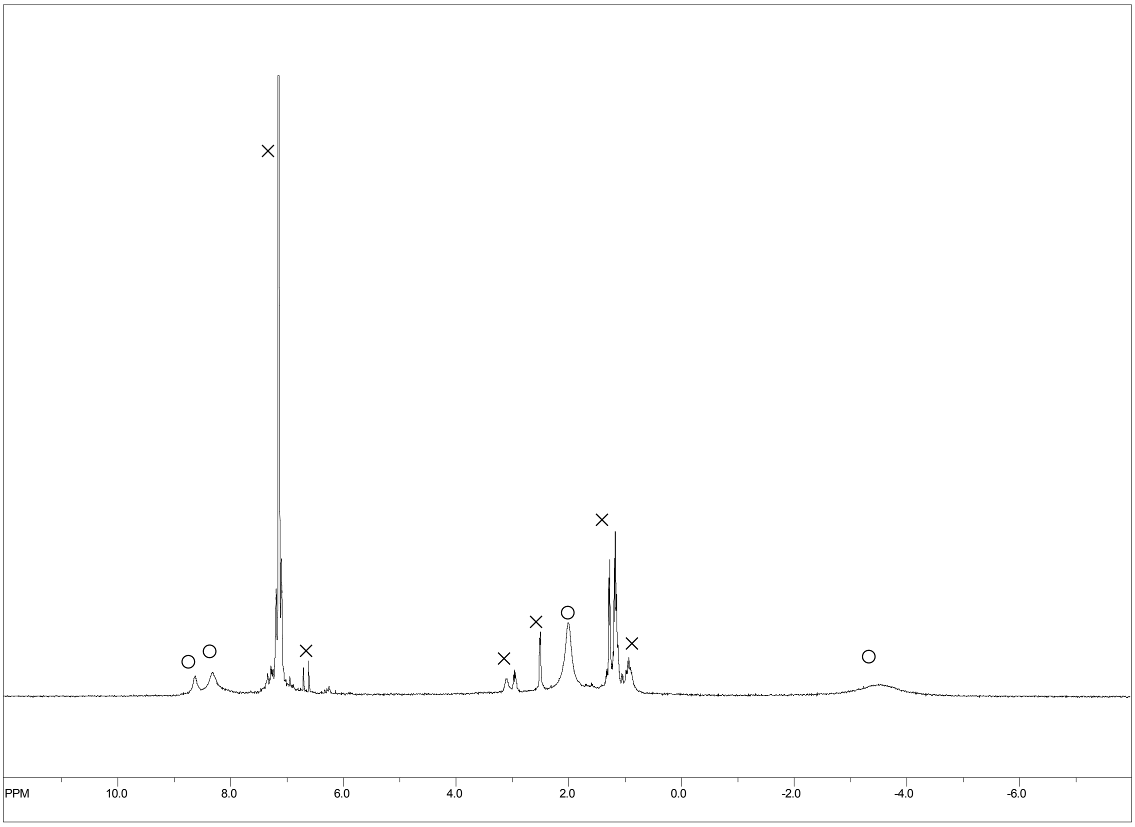

Figure S-2-1 ^{1}H NMR (400 MHz, C_6D_6) spectra for isolated **2** (○) in the presence of free IPr and small amount of **3** (×) which was generated by the equilibrium

S-3 Detection of 4,4'-dimethylbiphenyl by ^{1}H NMR and GS-MS measurements

In the reaction of Ni(IPr)$_2$ (**1**) with *p*-chlorotoluene, the complex **2** and aryl radical may form, according to the Kochi's report.[3] Most of the aryl radical in toluene at room temperature may react with each other to form arene and biaryl, 4,4'-dimethylbiphenyl, which can be detected in the ^{1}H NMR spectrum (**S-3-1**) of the crude mixture and also in the GC-MS spectra (**S-3-2**).

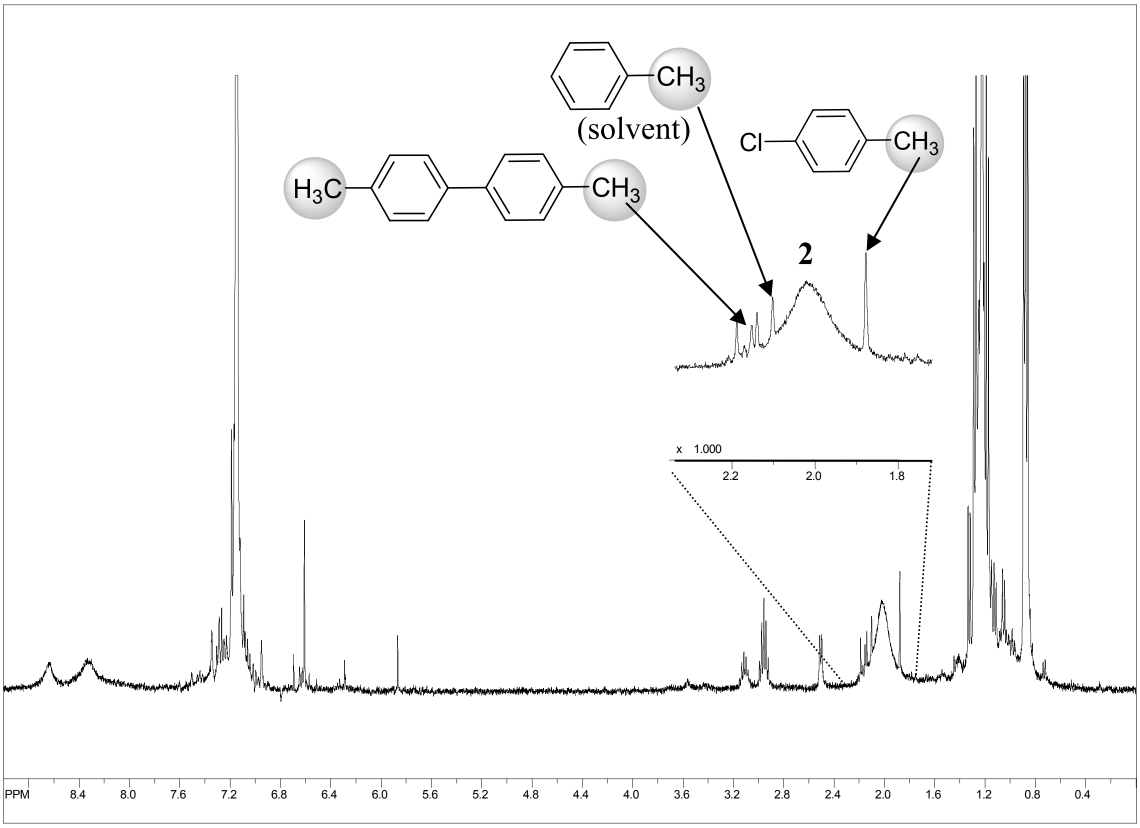

Figure S-3-1. ^{1}H NMR spectrum for the crude mixture of the reaction of **1** with 4-chlorotoluene

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[3] J. K. Kochi, *Pure & Appl. Chem.* 1980, **52**, 571-605.

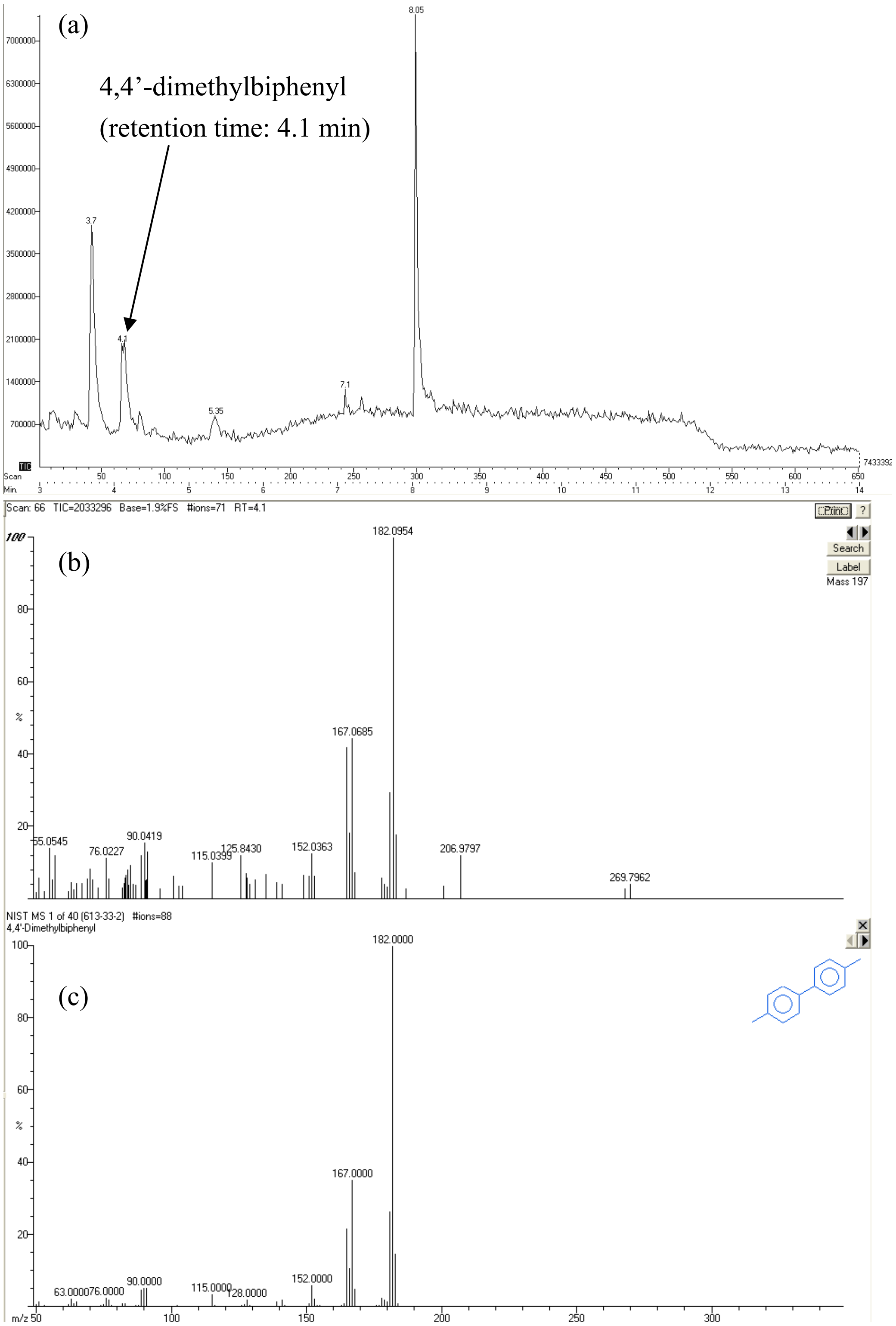
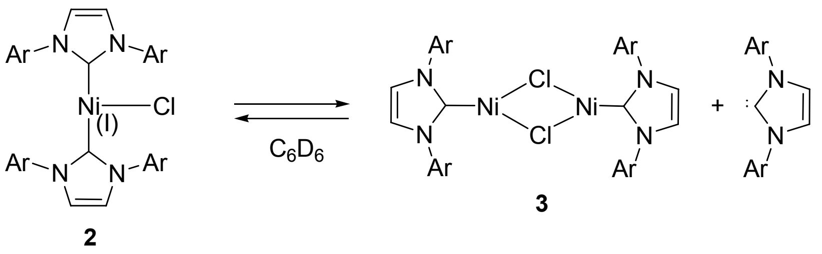


Figure S-3-2. GC-MS spectra for organic products in the reaction of **1** with 4-chlorotoluene in toluene: (a) GC spectrum, (b) MS spectrum for 4,4'-dimethylbiphenyl detected in the mixture, (c) MS spectrum for 4,4'-dimethylbiphenyl in the NIST MS data base.

S-4 Evidence for the equilibrium between **2** and [Ni(IPr)(μ-Cl)]$_2$ (**3**)

We observed that dissolution of the crystals of **2** in C_6D_6 resulted in the formation of the dinickel μ-chloride **3** and IPr to some extent. This suggests that equilibrium exist in solution between **2** and **3** + IPr as show in the Scheme S-4-1. In order to confirm this equilibrium, we added IPr to the solution of **3**, which was synthesized according to the literature ($NiCl_2$(dme) + Ni(cod)$_2$ + IPr).[4] As a result, the complex **3** completely disappeared and instead, **2** generated, as IPr was added to the solution of **3**.



Scheme S-4-1

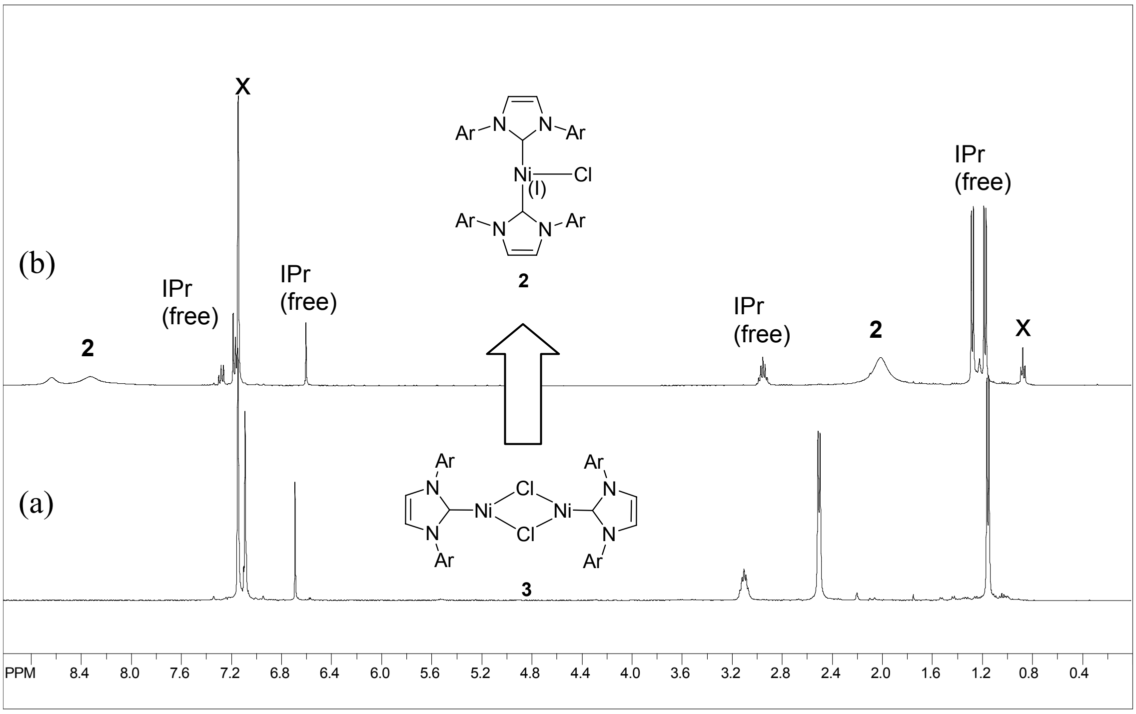


Figure S-4-1. ^{1}H NMR spectra for (a) the compound **3** and (b) that after addition of IPr to the solution of **3** showing complete disappearance of **3** and production of **2** in situ (see, **Figure S-2-1**, assigning signals for **2**).

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[4] B. R. Dible, M. S. Sigman, A. M. Arif, *Inorg. Chem.* 2005, **44**, 3774-3776.

S-5 Magnetic measurements of 2

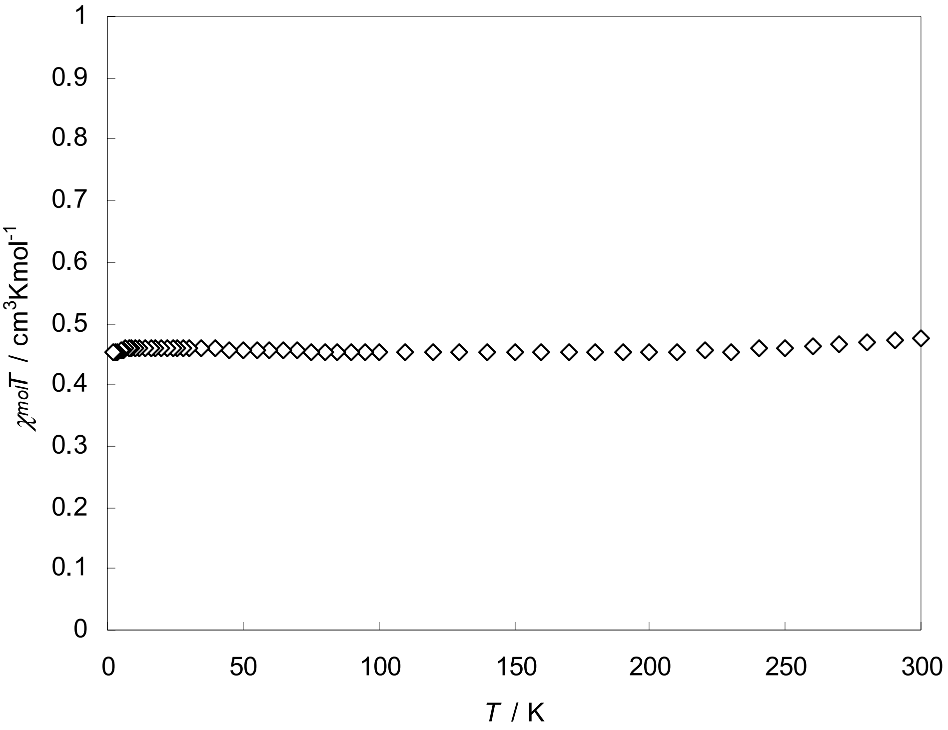

Figure S-5-1. χT-T plots for the compound **2**. At 2 K, the χT value was about 0.45 and the spin quantum number can be predicted to be 1/2. (Theoretical χT values (S = 1/2 and 2/2) are 0.375 and 1.00, respectively.)

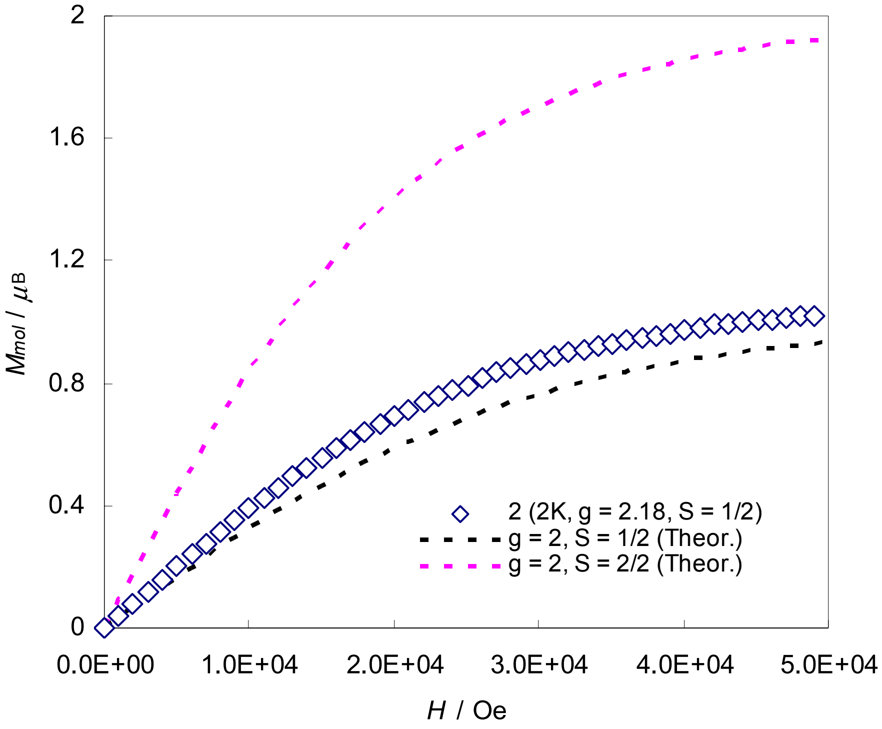

Figure S-5-2. Field-dependence of the magnetic moment of **2** at 2 K. Black dotted theoretical line (g = 2.00, S = 1/2), which is calculated with Brillouin Function, is close to the experimental line, showing that the spin quantum number of **2** is 1/2. Curve fitting with changing the g value revealed that the line at g = 2.18 is well consistent with the experimental line. The calculated χT value (S = 1/2 and g = 2.18) is 0.446, being agree with the experimental value (ca. 0.45 from Figure S-3-1).

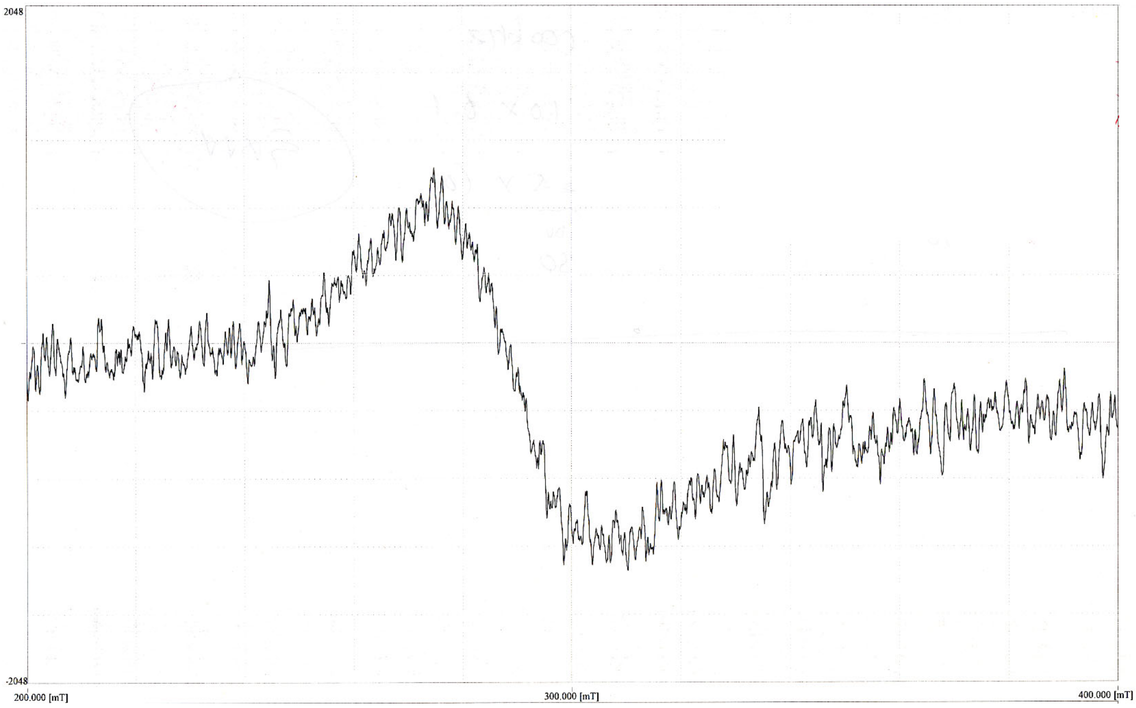

Figure S-5-3. ESR spectrum for **2** in toluene at 190 K. Because of troubles in the cooling system, we can only observe the spectra over the temperature.

S-6 DFT calculation of 2

DFT calculation for the structure of **2** was carried out with Gaussian 03 software on the Research Institute for Information Technology at Kyushu University. The B3LYP functional and 6-31G(d,p) basis set were used for the calculation. The 3-D coordinates of all the atoms given by the single-crystal X-ray diffraction study were used for the calculation. In the SOMO orbital, most of the unpaired electron is located at the d_{x2-y2} orbital of nickel (99.7%). Less than 0.3 % exists at the Ni-Cl σ^* and the NHC π^* orbital. That is, this unpaired electron does not make thermally unstable of this complex at room temperature.

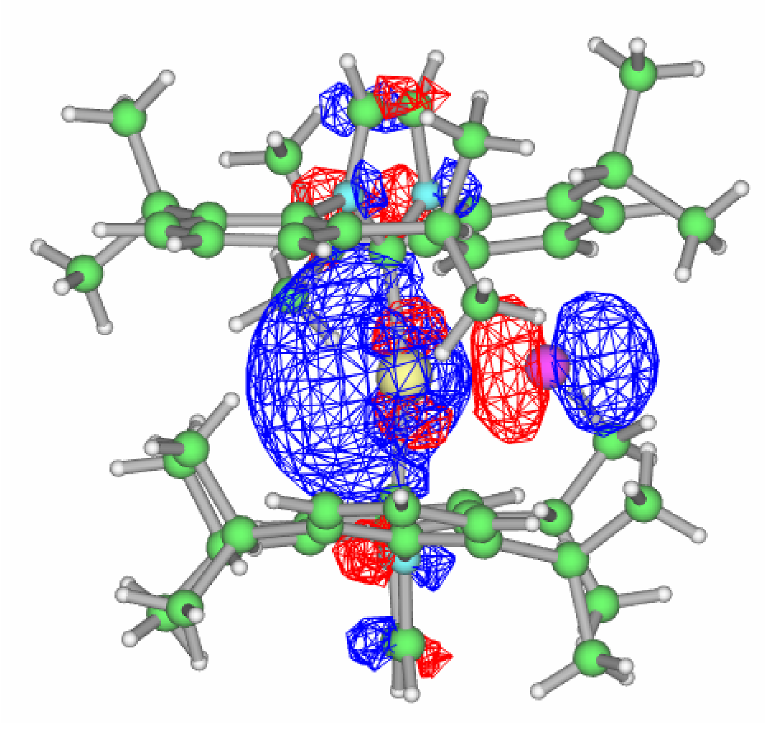

Figure S-4-1. SOMO orbital of **2** calculated with Gaussian03 (B3LYP 6-31G(d,p))

S-7 Single-crystal X-ray crystallography

Yellow single crystals of **2** (**2-THF** and **2-hexane**) for X-ray diffraction studies were grown at -30°C from the hexane and hexane/THF solutions, respectively. Both of the data was collected at 123 K on a RIGAKU Saturn CCD diffractometer with conforcal mirror using graphite monochromated Mo *K*α 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)[5] and refined by full-matrix least-squares fitting based on F^2 using the program SHELXL 97-2 PC version.[6] 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. The crystals (**2-THF** and **2-hexane**) contain the solvents, two THF molecules and one hexane molecule for one cell, respectively.

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[5] M. C. Burla,M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, SIR2002; 2003.

[6] G. M. Sheldrick, SHELXL97-2; 1997.