[Ni(Np$^{\#}$)(η^5-Cp)Cl]: Flexible, Sterically-Bulky, Well-Defined, Highly Reactive Complex for Nickel-Catalyzed Cross-Coupling

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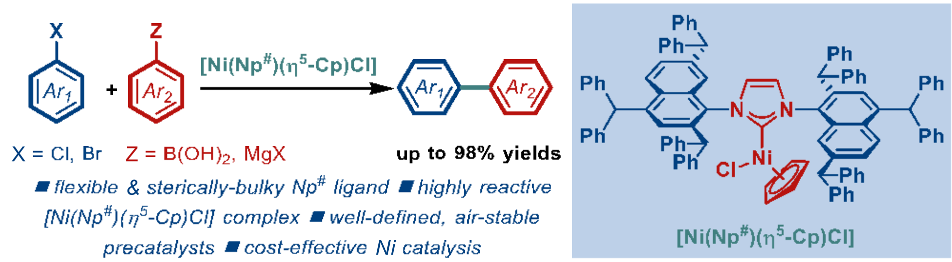
Supporting Information



ABSTRACT: Ni–NHCs (NHC = N-heterocyclic carbene) have become an increasingly important class of complexes in catalysis and organometallic chemistry owing to the beneficial features of nickel as an abundant 3d metal. However, the development of well-defined and air-stable Ni–NHC complexes for cross-coupling has been more challenging than with Pd–NHC catalysis because of less defined reactivity trends of NHC ancillary ligands coordinated to Ni. Herein, we report the synthesis and catalytic activity of well-defined [Ni(NHC)(η^5-Cp)Cl] complexes bearing recently commercialized IPr$^{\#}$ family of ligands (Sigma Aldrich) and versatile cyclopentadienyl throw-away ligand. The NHC ligands, IPr$^{\#}$, Np$^{\#}$ and BIAN-IPr$^{\#}$, are prepared by robust and modular peralkylation of anilines. Most crucially, we identified [Ni(Np$^{\#}$)(η^5-Cp)Cl] as a highly reactive [Ni(NHC)(η^5-Cp)Cl] complex, with the reactivity outperforming the classical [Ni(IPr)(η^5-Cp)Cl] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). These [Ni(NHC)(η^5-Cp)Cl] precatalysts were employed in the Suzuki and Kumada cross-coupling of aryl chlorides and aryl bromides. Computational studies were conducted to determine steric effect and bond order analysis. Considering the attractive features of well-defined Ni–NHCs, we anticipate that this class of bulky and flexible Ni–NHC catalysts will find broad application in organic synthesis and catalysis.

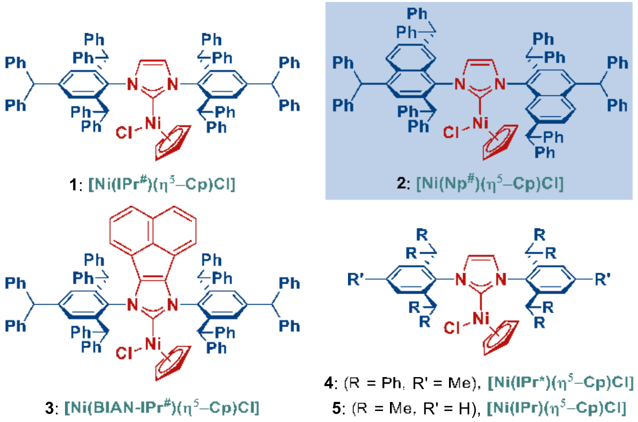
Introduction

The past three decades have witnessed a tremendous success of N-heterocyclic carbene (NHC) ligands in catalysis and organometallic chemistry.[1-3] The major impact of NHC ligands in transition-metal-catalysis arises from the unique electronic[4] and steric[5] properties of NHCs as well as diversity of their structural topology,[6] which collective-ly permit to support various metals at different oxidation states.[7] In this context, the utility of flexible steric bulk of NHC ligands has been a major driving force to establish effective catalysts for cross-coupling reactions.[3–5]

Simultaneously, Ni–NHC complexes have recently garnered significant attention as homogeneous catalysts in organic synthesis owing to the advantages of Ni as an abundant and inexpensive 3d transition metal.[8-10] However, despite intensive research efforts, there are still few examples of well-defined and air-stable Ni(II)–NHC precatalysts for cross-coupling reactions.[8,9] Out of several classes of well-defined Ni(II)–NHCs available,[9–13] [Ni(NHC)(η^5-Cp)Cl] complexes supported by the cyclopentadienyl throw-away ligand are considered particularly attractive owing to the ease of synthesis, high air- and moisture-stability and facile activation to Ni(0).[10–12]

The major challenge in developing new [Ni(NHC)(η^5-Cp)Cl] complexes includes less defined reactivity trends in NHC ligands coordinated to Ni, especially as compared with Pd–NHC catalysis[3–5] where IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) is generally considered as the 'first-choice' privileged ligand for catalysis.[14] However, it is worth pointing out that some of the reactivity of IPr have been superseded by IPr* and IPent and derivatives, especially in the field of palladium catalysis.[1-3,15] Further challenges in developing new Ni–NHC catalysts include shorter life-time of active catalyst species and high activation barrier to generate the active Ni catalyst.[8,9] Consequently, these challenges have created an attractive research frontier to access new well-defined Ni–NHCs for catalysis research.[9–13]

Recently, in collaboration with Sigma Aldrich, our laboratory has commercialized IPr$^{\#}$ family of ligands (SigmaAldrich).[15] The commercial availability of the ligands significantly decreases to barrier to use the ligands by the synthetic community.[15] These bulky and flexible NHC ligands, IPr$^{\#}$, Np$^{\#}$ and BIAN-IPr$^{\#}$, based on imidazol-2-ylidene scaffold are synthesized by a robust and modular peralkylation of anilines, which facilitates access to this class of ligands. This peralkylation permits for a facile synthetic access, while the remote substitution stabilizes the N-Ar wingtip rotation and opens up previously unexplored steric space of NHC ligands. This IPr$^{\#}$ class of sterically-hindered and flexible NHCs has been utilized to access [Pd(NHC)(cin)Cl] complexes for C–Cl, C–N, C–O, C–S and C–H cross-coupling.[15] Here, as a part of our program in catalyst development,[16] we report the synthesis and catalytic activity of well-defined [Ni(NHC)(η^5-Cp)Cl] complexes bearing IPr$^{\#}$ family of ligands and versatile cyclopentadienyl throw-away ligand. Most crucially, we identified [Ni(Np$^{\#}$)(η^5-Cp)Cl] as a highly reactive [Ni(NHC)(η^5-Cp)Cl] complex, with the reactivity outperforming [Ni(IPr)(η^5-Cp)Cl].


1: [Ni(IPr$^{\#}$)(η^5–Cp)Cl]

2: [Ni(Np$^{\#}$)(η^5–Cp)Cl]

3: [Ni(BIAN-IPr$^{\#}$)(η^5–Cp)Cl]

4: (R = Ph, R' = Me), [Ni(IPr*)(η^5–Cp)Cl]

5: (R = Me, R' = H), [Ni(IPr)(η^5–Cp)Cl]

Figure 1. Well-defined, air-stable [Ni(NHC)(η^5-Cp)Cl] complexes.

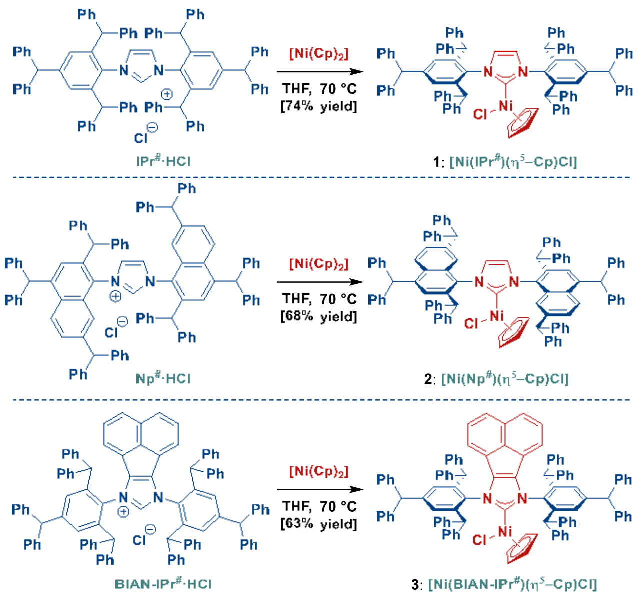
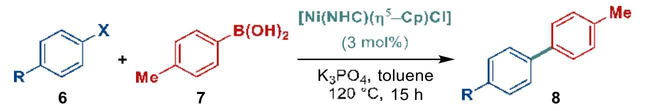


Figure 2. Synthesis of well-defined, air-stable [Ni(NHC)(η^5-Cp)Cl] complexes **1-3**. See reference 15 for availability of IPr$^{\#}$HCl, Np$^{\#}$HCl, BIAN-IPr$^{\#}$HCl.

Results and Discussion

Design. [Ni(NHC)(η^5-Cp)Cl] catalysts selected for this study are shown in Figure 1. The IPr$^{\#}$ family of ligands consists of the parent IPr$^{\#}$ ligand, flexible Np$^{\#}$ ligand and the bulky BIAN-IPr$^{\#}$. The classical IPr and the more bulky IPr* ligands were selected for comparison.[10,17] Previous studies have shown that [Ni(IMes)(η^5-Cp)Cl] is less reactive than [Ni(IPr)(η^5-Cp)Cl] in [Ni(NHC)(η^5-Cp)Cl] complexes.[12b] The goal of the study was to compare the catalytic activity of [Ni(NHC)(η^5-Cp)Cl] within the IPr$^{\#}$ class and with the established IPr and IPr* ligands.

Table 1. Suzuki–Miyaura Cross-Coupling Using [Ni(NHC)(η^5-Cp)Cl] Complexes 1–5[a]



entry	Ar-X	catalyst	yield (%)[b]
1	4-Ac-C_6H_4-Cl	**1**: [Ni(IPr$^{\#}$)(η^5-Cp)Cl]	47
2	4-Ac- C_6H_4-Cl	**2**: [Ni(Np$^{\#}$)(η^5-Cp)Cl]	91
3	4-Ac- C_6H_4-Cl	**3**: [Ni(BIAN-IPr$^{\#}$)(η^5-Cp)Cl]	5
4	4-Ac- C_6H_4-Cl	**4**: [Ni(IPr*)(η^5-Cp)Cl]	41
5	4-Ac- C_6H_4-Cl	**5**: [Ni(IPr)(η^5-Cp)Cl]	65
6	4-MeO-C_6H_4-Br	**1**: [Ni(IPr$^{\#}$)(η^5-Cp)Cl]	59
7	4-MeO-C_6H_4-Br	**2**: [Ni(Np$^{\#}$)(η^5-Cp)Cl]	>98
8	4-MeO-C_6H_4-Br	**3**: [Ni(BIAN-IPr$^{\#}$)(η^5-Cp)Cl]	6
9	4-MeO-C_6H_4-Br	**4**: [Ni(IPr*)(η^5-Cp)Cl]	48
10	4-MeO-C_6H_4-Br	**5**: [Ni(IPr)(η^5-Cp)Cl]	50

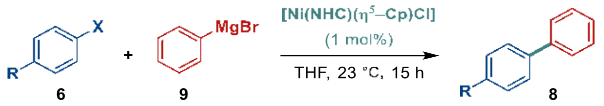
[a] Conditions: R-C_6H_4-X (1.0 equiv), Ar-B(OH)$_2$ (2.0 equiv), catalyst (3 mol%), K_3PO_4(2.6 equiv), toluene (0.2 M), 120 °C, 15 h. [b] GC/^{1}H NMR yields.

Catalyst Synthesis. Well-defined [Ni(NHC)(η^5-Cp)Cl] complexes (**1-3**) bearing IPr$^{\#}$ (**1**), Np$^{\#}$ (**2**) and BIAN-IPr$^{\#}$ (**3**) ligands were synthesized by the reaction between NHC·HCl salt and [Ni(η^5-Cp)$_2$] in THF at 70 °C in 63-74% yields (Figure 2).[10] The known [Ni(NHC)(η^5-Cp)Cl] catalysts with IPr* (**4**) and IPr ligands (**5**) were synthesized by the same method.[10] [Ni(NHC)(η^5-Cp)Cl] complexes **1–3** were isolated after trituration with cold ether. All complexes were found to be stable to air and moisture.

Catalyst Evaluation. With access to [Ni(NHC)(η^5-Cp)Cl] precatalysts, we next evaluated their catalytic activity in the Suzuki-Miyaura cross-coupling (Table 1).[11,12b] We have used standard conditions for testing the reactivity of [Ni(NHC)(η^5-Cp)Cl] complexes (toluene, K_3PO_4) with temperature modification (120 °C). In our previous studies, we found these conditions to be more effective for evaluating the reactivity of [Ni(NHC)(η^5-Cp)Cl] in cross-coupling.[16f,12f,h] The reaction time was not optimized.

We first tested 4-chloroacetophenone as a model and less reactive substrate than the typically used 4-bromoacetophenone (Table 1, entries 1-5).[11,12b] We determined that [Ni(IPr$^{\#}$)(η^5-Cp)Cl] (**1**) and [Ni(IPr*)(η^5-Cp)Cl] (**4**) promoted close to 50% conversion to the biaryl, with the [Ni(IPr$^{\#}$)(η^5-Cp)Cl] catalyst (**1**) (Table 1, entry 1) more reactive than [Ni(IPr*)(η^5-Cp)Cl] (**4**) (Table 1, entry 4). Interestingly, [Ni(Np$^{\#}$)(η^5-Cp)Cl] (**2**) delivered excellent yield (Table 1, entry 2), while precatalyst [Ni(BIAN-IPr$^{\#}$)(η^5-Cp)Cl] (**3**) was ineffective for this reaction (Table 1, entry 3). Furthermore, precatalyst [Ni(IPr)(η^5-Cp)Cl] (**5**) was less reactive than [Ni(Np$^{\#}$)(η^5-Cp)Cl] (**2**) (Table 1, entry 5).

Table 2. Kumada Cross-Coupling Using [Ni(NHC)(η^5-Cp)Cl] Complexes 1–5[a]



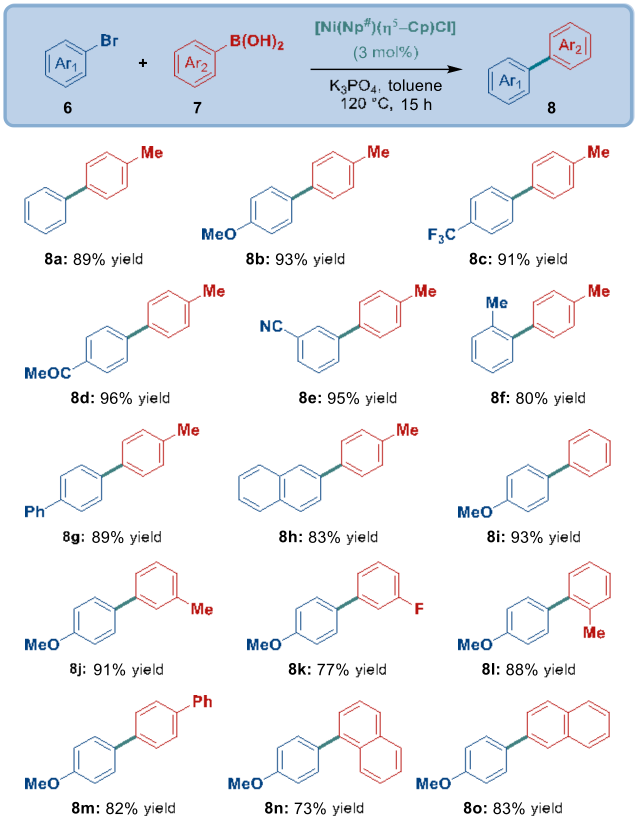
entry	Ar-X	catalyst	yield (%)[b]
1	4-MeO-C$_6$H$_4$-Cl	**1**: [Ni(IPr$^{\#}$)(η^5-Cp)Cl]	64
2	4-MeO-C$_6$H$_4$-Cl	**2**: [Ni(Np$^{\#}$)(η^5-Cp)Cl]	>98
3	4-MeO-C$_6$H$_4$-Cl	**3**: [Ni(BIAN-IPr$^{\#}$)(η^5-Cp)Cl]	36
4	4-MeO-C$_6$H$_4$-Cl	**4**: [Ni(IPr*)(η^5-Cp)Cl]	51
5	4-MeO-C$_6$H$_4$-Cl	**5**: [Ni(IPr)(η^5-Cp)Cl]	56
6	4-MeO-C$_6$H$_4$-Br	**1**: [Ni(IPr$^{\#}$)(η^5-Cp)Cl]	57
7	4-MeO-C$_6$H$_4$-Br	**2**: [Ni(Np$^{\#}$)(η^5-Cp)Cl]	>98
8	4-MeO-C$_6$H$_4$-Br	**3**: [Ni(BIAN-IPr$^{\#}$)(η^5-Cp)Cl]	15
9	4-MeO-C$_6$H$_4$-Br	**4**: [Ni(IPr*)(η^5-Cp)Cl]	59
10	4-MeO-C$_6$H$_4$-Br	**5**: [Ni(IPr)(η^5-Cp)Cl]	77

[a] Conditions: R-C$_6$H$_4$-X(1.0 equiv), Ar-MgBr (2.0 equiv), catalyst (1 mol%), THF (0.1 M), 23°C, 15 h. [b] GC/^{1}H NMR yields.

Next, we tested the catalytic activity of [Ni(NHC)(η^5-Cp)Cl] complexes **1-5** in the Suzuki-Miyaura using an electronically-deactivated 4-bromoanisole substrate, which again is less reactive than the typically used 4-bromoacetophenone (Table 1, entries 6-10).[11,12b] These studies showed a similar order of activity as in the cross-coupling of 4-bromoanisole, with precatalyst [Ni(Np$^{\#}$)(η^5-Cp)Cl] (**2**) outperforming all other catalysts and delivering quantitative yield (Table 1, entry 7). Thus, the order of catalytic reactivity in the Suzuki-Miyaura cross-coupling is as follows: *[Ni(Np$^{\#}$)(η^5-Cp)Cl]* (**2**) >> *[Ni(IPr)(η^5-Cp)Cl]* (**5**) ≈ *[Ni(IPr$^{\#}$)(η^5-Cp)Cl]* (**1**) > *[Ni(IPr*)(η^5-Cp)Cl]* (**4**) >> *[Ni(BIAN-IPr$^{\#}$)(η^5-Cp)Cl]* (**3**). We further note that the reactivity of catalyst [Ni(Np$^{\#}$)(η^5-Cp)Cl] (**2**) using deactivated 4-chloroanisole substrate resulted in a promising 30% yield under these conditions (not shown).

Having determined high reactivity of [Ni(Np$^{\#}$)(η^5-Cp)Cl] complex in the Suzuki–Miyaura cross-coupling, we evaluated its activity in Kumada cross-coupling with the goal of testing if this catalyst is compatible with electronically-deactivated chloroarenes as compatible substrates for cross-coupling (Table 2).[18] In the cross-coupling of 4-chloroanisole (Table 2, entries 1-5), we found that [Ni(NHC)(η^5-Cp)Cl] precatalysts showed similar order of activity as in the Suzuki cross-coupling, with [Ni(Np$^{\#}$)(η^5-Cp)Cl] (**2**) as by far the most effective catalyst (Table 2, entry 2). We further evaluated the cross-coupling of 4-bromoanisole as a representative electronically-deactivated bromoarene (Table 2, entries 6-10). Likewise, we found that [Ni(Np$^{\#}$)(η^5-Cp)Cl] (**2**) is the most effective catalyst. Thus, the order of activity of [Ni(NHC)(η^5-Cp)Cl] in the Kumada cross-coupling reflects the reactivity in the Suzuki–Miyaura cross-coupling: *[Ni(Np$^{\#}$)(η^5-Cp)Cl]* (**2**) >> *[Ni(IPr)(η^5-Cp)Cl]* (**5**) ≈ *[Ni(IPr$^{\#}$)(η^5-Cp)Cl]* (**1**) > *[Ni(IPr*)(η^5-Cp)Cl]* (**4**) >> *[Ni(BIAN-IPr$^{\#}$)(η^5-Cp)Cl]* (**3**).

Scheme 1. Substrate Scope for Suzuki–Miyaura Cross-Coupling using [Ni(Np$^{\#}$)(η^5-Cp)Cl] (2)[a]

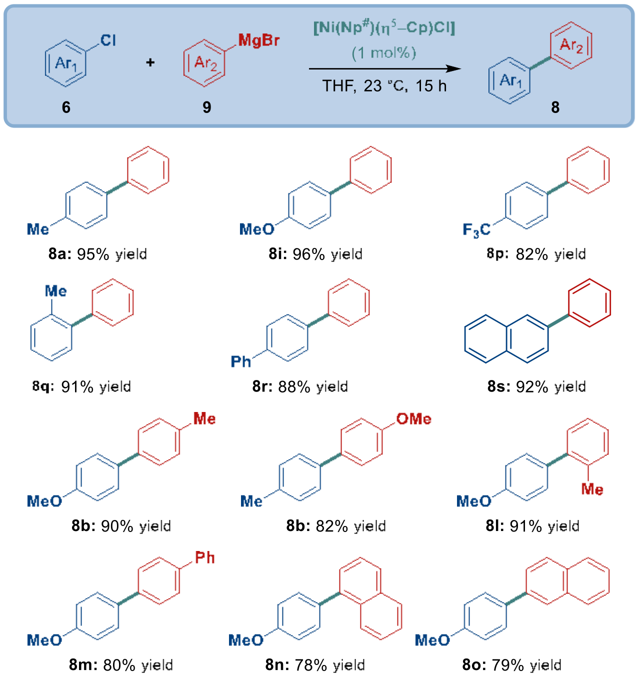


[a] Conditions: Ar-Br (1.0 equiv), Ar-B(OH)$_2$ (2.0 equiv), catalyst (3 mol%), K$_3$PO$_4$(2.6 equiv), toluene (0.2 M), 120 °C, 15 h.

Substrate Scope. Having identified [Ni(Np$^{\#}$)(η^5-Cp)Cl] (**2**) as a highly reactive catalyst, the scope of the Suzuki-Miyaura cross-coupling was briefly investigated (Scheme 1). As shown in Scheme 1, [Ni(Np$^{\#}$)(η^5-Cp)Cl] catalyst is effective in promoting the Suzuki cross-coupling of a wide range of aryl bromides, including electron-neutral (**8a**), electron-rich (**8b**) as well as electron-deficient substrates (**8c–8e**). Importantly, [Ni(Np$^{\#}$)(η^5-Cp)Cl] catalyst is compatible with sensitive functional groups, such as ketones (**8d**) and cyano (**8e**), which are often problematic using strongly basic conditions. Furthermore, ortho-sterically-hindered substrates (**8f**) can also be utilized using this catalyst. Finally, we were pleased to find that this catalyst is also compatible with polyaromatic aryl bromides, such as 4-biphenyl (**8g**) and 2-napthyl (**8h**). Next, the activity of [Ni(Np$^{\#}$)(η^5-Cp)Cl] precatalyst in the Suzuki-Miyaura cross-coupling using various boronic acids was investigated using electronically-deactivated 4-bromoanisole. We found that [Ni(Np$^{\#}$)(η^5-Cp)Cl] is capable of promoting cross-coupling using electronically-neutral (**8i**, **8j**) and electron-deficient (**8k**) aryl boronic acids. Furthermore, sterically-hindered boronic acids (**8l**) are competent substrates. Finally, polyaromatic aryl boronic acids, such as, 4-biphenyl (**8m**), sterically-hindered 1-napthyl (**8n**) and 2-

napthyl (**8o**) can be successfully cross-coupled using $[Ni(Np^{\#})(\eta^5\text{-}Cp)Cl]$ to deliver conjugated biaryls.

Scheme 2. Substrate Scope for Kumada Cross-Coupling using $[Ni(Np^{\#})(\eta^5\text{-}Cp)Cl]$ (2)[a]



[a]Conditions: Ar-Cl (1.0 equiv), Ar-MgBr (2.0 equiv), catalyst (1 mol%), THF (0.1 M), 23°C, 15 h.

Next, we evaluated the scope of Kumada cross-coupling using $[Ni(Np^{\#})(\eta^5\text{-}Cp)Cl]$ (Scheme 2). Pleasingly, we found that this catalyst can be used for Kumada cross-coupling using electronically-neutral (**8a**), electron-rich (**8i**) and electron-deficient (**8p**) aryl chlorides. Furthermore, ortho-substituted substrates (**8f**) as well as polyaromatic aryl halides, such as 4-biphenyl (**8g**) and 2-napthyl (**8h**) can be tolerated. The scope of arylmagnesium bromides was also briefly investigated using 4-chloroanisole as a representative substrate (Scheme 2). We are pleased to find that $[Ni(Np^{\#})(\eta^5\text{-}Cp)Cl]$ is efficient for various arylmagnesium bromides, including electronically-neutral (**8b**), electron-rich (**8b**) and sterically-hindered (**8i**). Furthermore, polycyclic arylmagnesium-bromides, such as 4-biphenyl (**8m**) and naphthyl (**8n-8o**) can be readily employed.

Preliminary studies using sterically-hindered halides and nucleophiles indicate that in the Suzuki cross-coupling di-ortho-substituted halides show promising reactivity (Mes-Br/4-Tol-$B(OH)_2$, 25% yield) (not shown), while mono-substituted halides and boronic acids are tolerated (Scheme 1, **8f**, **8l**). Furthermore, di-ortho-substituted boronic acids are not tolerated (4-Mes-$B(OH)_2$, <5% yield). In contrast, in the Kumada coupling, di-ortho-substituted halides (2,6-Me_2-C_6H_3-Cl/PhMgBr, 67% yield) and di-ortho-substituted organometallics show good reactivity (4-Tol-Cl/MesMgBr, 64% yield). Coordinating heterocycles, such as pyridines are not tolerated. Further studies to expand the scope are underway, and these studies will be reported in due course.

Steric and Electronic Effect. To gain insight into the steric and electronic properties of $[Ni(NHC)(\eta^5\text{-}Cp)Cl]$ complexes evaluated in this study, computational studies were conducted. Note that Np# ligand is asymmetric, affording anti (rac) and syn (meso) conformation of $[Ni(Np^{\#})(\eta^5\text{-}Cp)Cl]$.[19] Free carbene, anti-Np#, is more stable than meso-Np# (0.56 kcal/mol, B3LYP 6-311++g(d,p)).[15]

Steric Effect. First, to gain insight into the steric impact of NHC ligands in $[Ni(NHC)(\eta^5\text{-}Cp)Cl]$ complexes, the percent buried volume (%V_{bur}) was calculated using the method by Cavallo from the optimized structures of complexes **1**, **2**, **4** and **5** (Figure 3).[5] These studies determined the %V_{bur} of NHC in $[Ni(IPr^{\#})(\eta^5\text{-}Cp)Cl]$ (**1**) as 39.3% (SW, 46.0%; NW, 27.9%; NE, 53.6%; SE, 29.7%) and in $[Ni(Np^{\#})(\eta^5\text{-}Cp)Cl]$ (**2**) as 34.7% (*anti*: SW, 29.1%; NW, 40.4%; NE, 31.8%; SE, 37.3%) and 36.7% (*syn*: SW, 40.2%; NW, 29.7%; NE, 44.6%; SE, 32.1%). These values can be compared with the %V_{bur} of 36.6% (SW, 31.8%; NW, 43.9%; NE, 30.2%; SE, 40.5%) for complex $[Ni(IPr^{*})(\eta^5\text{-}Cp)Cl]$ (**4**) and 35.0% (SW, 33.7%; NW, 37.0%; NE, 33.4%; SE, 36.0%) for complex $[Ni(IPr)(\eta^5\text{-}Cp)Cl]$ (**5**). The quadrant distribution in $[Ni(Np^{\#})(\eta^5\text{-}Cp)Cl]$ (**2**) indicates significant flexibility of the Np# ligand on the Ni center.

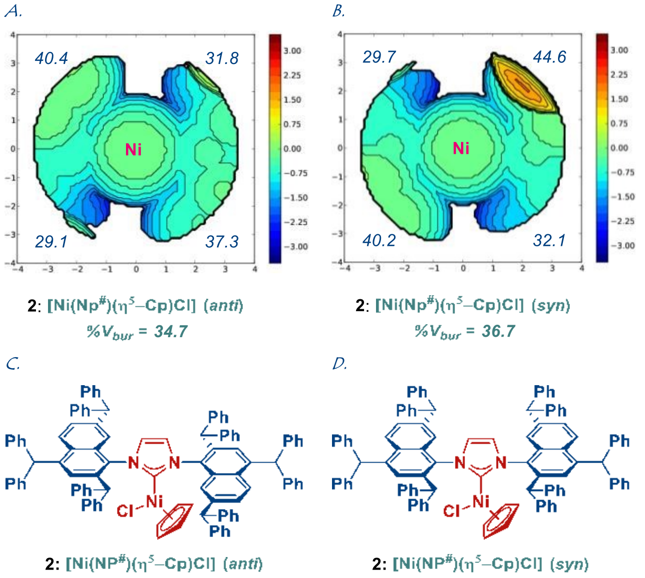


Figure 3. Topographical steric maps of $[Ni(Np^{\#})(\eta^5\text{-}Cp)Cl]$ (**2**); (A) *anti*; (B) *syn*; showing %V_{bur} per quadrant (B3LYP 6-311++g(d,p)). Structures of $[Ni(Np^{\#})(\eta^5\text{-}Cp)Cl]$ (**2**): *anti* (C); *syn* (D).

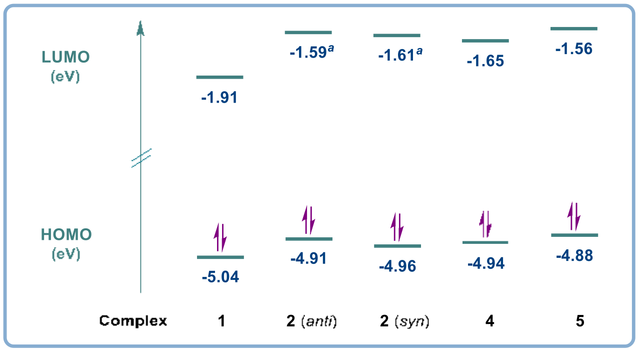


Figure 4. Energy diagram (eV) for frontier orbital of complexes of [Ni(IPr$^{\#}$)(η^5-Cp)Cl] (**1**), [Ni(Np$^{\#}$)(η^5-Cp)Cl] (**2**), [Ni(IPr*)(η^5-Cp)Cl] (**4**), [Ni(IPr)(η^5-Cp)Cl] (**5**) (B3LYP 6-311++g(d,p)).

Electronic Effect. To understand electronic properties of [Ni(NHC)(η^5-Cp)Cl] complexes, frontier molecular orbitals were calculated (Figure 4). The studies showed the HOMO of [Ni(IPr$^{\#}$)(η^5-Cp)Cl] (**1**) (-5.04 eV), [Ni(Np$^{\#}$)(η^5-Cp)Cl] (**2**) (*anti*: -4.91 eV; *syn*: -4.96 eV), [Ni(IPr*)(η^5-Cp)Cl] (**4**) (-4.94 eV) and [Ni(IPr)(η^5-Cp)Cl] (**5**) (-4.88 eV) in a similar range. In contrast, the LUMO of [Ni(IPr$^{\#}$)(η^5-Cp)Cl] (**1**) (-1.91 eV), [Ni(Np$^{\#}$)(η^5-Cp)Cl] (**2**) (*anti*: -1.59 eV; *syn*: -1.61 eV), [Ni(IPr*)(η^5-Cp)Cl] (**4**) (-1.65 eV) and [Ni(IPr)(η^5-Cp)Cl] (**5**) (-1.56 eV) (LUMO+2 of **2** due to required symmetry) showed more variation. Complex [Ni(IPr$^{\#}$)(η^5-Cp)Cl] (**1**) features the lowest energy for HOMO and LUMO, and the lowest energy gap (3.13 eV).

To further understand the relative strength of metal-ligand bond in [Ni(NHC)(η^5-Cp)Cl] complexes, NBO analysis was performed (Table 3).[20] The Wiberg bond orders for the Ni–NHC bond in [Ni(IPr$^{\#}$)(η^5-Cp)Cl] (**1**) (Ni–C$_{(carbene)}$, 0.6304; Ni–Cl, 0.6917) and in [Ni(Np$^{\#}$)(η^5-Cp)Cl] (**2**) (Ni–C$_{(carbene)}$, 0.6497 (*anti*), 0.6496 (*syn*); Ni–Cl, 0.6644 (*anti*), 0.6791 (*syn*)) can be compared with [Ni(IPr*)(η^5-Cp)Cl] (**4**) (Ni–C$_{(carbene)}$, 0.6409; Ni-Cl, 0.6658) and [Ni(IPr)(η^5-Cp)Cl] (**5**) (Ni–C$_{(carbene)}$, 0.6494; Ni–Cl, 0.6995). The studies showed that Ni–carbene bond in **2** is stronger than in other tested complexes. The syn conformation of [Ni(Np$^{\#}$)(η^5-Cp)Cl] (**2**) showed the lowest Ni–Cl bond order. Altogether, the data suggest faster activation and longer lifetime of [Ni(NHC)(η^5-Cp)Cl] in combination with the flexible steric bulk around the metal-center. It is worthwhile to point out that flexibility of N-Ar wingtips around the N–Ar axis (Figure 3C-D) is a unique feature of this class of catalysts.[1-3] We think that both isomers contribute to the high reactivity of the complex by creating sterically flexible environment capable of accommodating different substrates and promoting elementary steps of the catalytic cycle. Further studies to determine the effect of conformation on the reactivity, including locking the conformation as single isomers are underway.

Table 3. Bond Orders of Complexes 1, 2, 4 and 5

entry	complex	Ni–C$_{(carbene)}$	Ni–Cl
1	**1**: [Ni(IPr$^{\#}$)(η^5-Cp)Cl]	0.6304	0.6917
2	**2**: [Ni(Np$^{\#}$)(η^5-Cp)Cl] (*anti*)	0.6497	0.6644
3	**2**: [Ni(Np$^{\#}$)(η^5-Cp)Cl] (*syn*)	0.6496	0.6791
4	**4**: [Ni(IPr*)(η^5-Cp)Cl]	0.6409	0.6658
5	**5**: [Ni(IPr)(η^5-Cp)Cl]	0.6494	0.6995

In summary, in this study we have reported the synthesis and catalytic activity of well-defined [Ni(NHC)(η^5-Cp)Cl] complexes featuring recently commercialized IPr$^{\#}$ family of ligands and versatile cyclopentadienyl throw-away ligand. Most crucially, this study identified [Ni(Np$^{\#}$)(η^5-Cp)Cl] as a highly reactive [Ni(NHC) (η^5-Cp)Cl] complex. The most reactive [Ni(Np$^{\#}$)CpCl] is well-defined, air- and bench-stable and is based on the modular IPr$^{\#}$ aniline peralkylation approach. This class of bulky, flexible, air-stable and well-defined Ni(II)–NHC catalysts represents an attractive ligand entry for wide application in organic synthesis and catalysis.

ASSOCIATED CONTENT

Supporting Information

Procedures and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare the following competing financial interest(s): Rutgers University has filed patent(s) on ligands and precatalysts described in this manuscript (US 62/958,565, Jan 8, 2020). Rutgers University may receive royalties from the ligands reported in this manuscript.

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