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SHORT COMMUNICATION

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A Catalyst with Two-Coordinate Nickel: Theoretical and Catalytic Studies

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Dedicated to Professor Marius Andruh on the occasion of his 60th birthday

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The bisadduct $(cAAC)_2Ni^{II}Cl_2$ [**1**; cAAC = cyclic (alkyl)(amino)carbene] was directly synthesized by treating cAAC with $NiCl_2$. Compound **1** was reduced to $(cAAC)_2Ni^0$ (**2**) by using lithium diisopropylamide or KC_8. Crystals of **2** were stable under an inert gas for several months and decomposed upon heating above 165 °C. On the basis of the calculated natural bond orbital charge values of the nickel atom in **2**, the oxidation state of nickel was determined to be between Ni^I and Ni^0 (+0.34). Theoretical calculations suggested a closed-shell singlet electronic configuration of **2** with little biradical character. Ab initio multiconfigurational C(R)ASSCF/CASPT2 calculations predicted a closed-shell singlet electronic configuration (Ni^0), whereas excited spin states possessed Ni^I character with unpaired electrons on neighboring carbon atoms. The catalytic activity of complex **2** was investigated for the homocoupling of various unactivated aryl chlorides/fluorides. The biaryls were obtained in good yields at moderate temperature. Theoretical studies showed that an intermediate containing Ni^{III} was more favored than one with Ni^{IV}.

Introduction

Compounds containing low-coordinate transition metal atoms have been the focus of great interest in the field of catalysis in recent times as a result of the presence of unsaturated coordination sites.[1] Such species can act as active catalysts.[1a] Recently, stable d^1–d^9 open-shell complexes[1b] with two-coordinate transition-metal ions were summarized, and their reactivities were explored.[1] N-Heterocyclic carbenes (NHCs) are also known to form two-coordinate metal (M) complexes (M = Ni^0, Pd^0, Cu^I, Co^I). However, they are not yet known to form stable mono- or bisadducts[2] upon reaction with NiX_2 (X = Cl, Br, I). $[(NHC)Ni(\mu\text{-}Cl)Cl]_2$, rather $(NHC)_2NiX_2$, have been prepared by different synthetic routes.[3] The bisadducts of NiX_2 are effective catalysts for various C–C cross-coupling reactions (Suzuki, Heck, Kumada, Negishi, and reductive Ullmann coupling).[3b] Thus, palladium compounds that also catalyze such reactions can alternatively be replaced by nickel–carbene complexes. Compounds such as $(NHC)Ni^{II}{=}N{-}R$,[4a] $(NHC)Ni^I(NH{-}R)$,[4b] and $(NHC)_2Ni^0$[5] with two-coordinate nickel atoms are known. $(NHC)_3Ni^0$ and $[(NHC)Ni^0]_2$ with three- and seven-coordinate nickel atoms, respectively, were also reported.[6] A few computational studies have been accomplished for the better understanding of the electronics of such species containing zero-valent nickel atoms.[5] Radius and Bickelhaupt[5e] performed a detailed study of the bonding situation of $(NHC)_2Ni^0$ derivatives by using energy decomposition analysis. They showed that the π interaction is about 43–32% of the total orbital interaction between Ni^0 and the NHC ligands.[5e] $(NHC)_2Ni^0$ compounds might be promising catalysts for unusual organic transformations.[7] However, none of the $(NHC)_2Ni^0$[5] compounds were prepared by utilizing $(NHC)_2Ni^{II}X_2$ as a pre-

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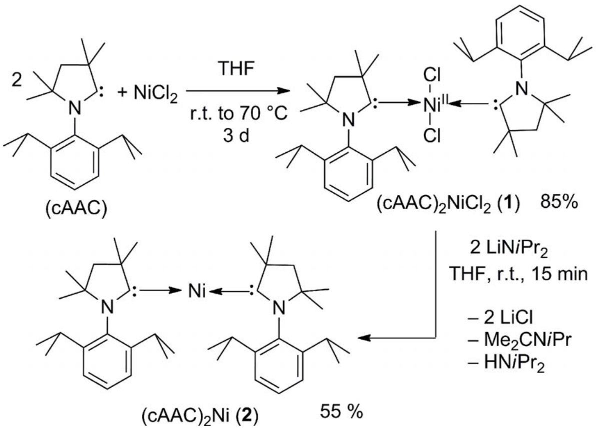
cursor. Instead, a reverse approach was applied for the preparation of $(NHC)_2Ni^{II}X_2$, $(NHC)_2Ni^{II}XPh$, and $(NHC)_2Ni^{I}X$.[3,8]

The carbene carbon atom in the NHC is bound to two σ-withdrawing and π-donating N atoms. However, in the case of a cyclic (alkyl)(amino)carbene (cAAC), one of the σ-withdrawing and π-donating N atoms is replaced by one σ-donating quaternary C atom. Thus, the cAAC becomes more nucleophilic but also more electrophilic than the NHC.[9] Hence, the use of a cAAC might be advantageous over an NHC for certain reactions. Herein, we report a direct synthesis of the bisadduct $(cAAC)_2Ni^{II}Cl_2$ (**1**) and its reduction to a singlet $(cAAC)_2Ni$ (**2**) with two-coordinate nickel(0) atom (Scheme 1). Theoretical investigations suggest that the first low-lying excited state of **2** possesses Ni^{I} character having a delocalized radical electron over two carbene carbon atoms. Magnetic susceptibility measurements and detailed theoretical calculations of **2** were performed to support the electronic scenario. Compound **2** acts as an efficient catalyst for the reductive homocoupling of aryl chlorides and fluorides through C–Cl and C–F bond activation at 50 °C.



Scheme 1. Synthetic strategy for compounds **1** and **2**.

Results and Discussion

The bisadduct $(cAAC)_2Ni^{II}Cl_2$ (**1**) was formed upon direct reaction of anhydrous $NiCl_2$ with the cAAC in a 1:2 molar ratio in THF. First, the formation of a yellow suspension was observed, which was heated to 70 °C for 3–4 h to obtain an orange-yellow slurry. The resultant solution was stirred at room temperature for an additional 2 d to obtain a clear red solution of **1**. For comparison reasons, a similar reaction was applied for a suspension of NHC {NHC = $C[N(2,4\text{-diisopropylphenyl})(CH)]_2$} and $NiCl_2$. However, the latter reaction failed to produce an NHC analogue of **1**. Compound **1** was crystallized from toluene as air-stable red rods in 85% yield. Furthermore, **1** was treated with lithium diisopropylamide (LDA) in a 1:2 molar ratio to form an immediate dark purple solution of $(cAAC)_2Ni$ (**2**). LDA generally serves as a strong base, but it can also act as a reducing agent.[10] The mass spectrum of this solution revealed the formation of $Me_2C{=}N\mathit{i}Pr$, which suggests that the dehalogenation of $(cAAC)_2Ni^{II}Cl_2$ (**1**) occurred through α-hydride transfer[10] from LDA to **1** by elimination of LiCl to form a biscarbene–Ni^{II} chlorohydride intermediate, and this intermediate then reductively eliminated HCl (Supporting Information) to give **2**. The latter is consumed by another equivalent of LDA to form $HN\mathit{i}Pr_2$ and LiCl. The formation of $HN\mathit{i}Pr_2$ was confirmed by mass spectrometry. The calculated complexation energy for the formation of $(cAAC)_2Ni^{II}Cl_2$ (**1**) from the cAAC and $NiCl_2$ is highly exothermic [$\Delta E_1 = -125.1\ \mathrm{kcal\,mol^{-1}}$; see Equation (1)] at the M06/def2-TZVPP//BP86/def2-SVP level of theory.[11,12] The reductive dehalogenation of **1** by 2 equiv. of LDA to $(cAAC)_2Ni$ (**2**) is also exothermic [$\Delta E_2 = -12.8\ \mathrm{kcal\,mol^{-1}}$; see Equation (2)]. Both of these reactions indicate the thermodynamic preference for the formation of complex **1** and its reductive dehalogenation by LDA to complex **2**.

$$2\ \mathrm{cAAC} + NiCl_2 \rightarrow (cAAC)_2Ni^{II}Cl_2\ (\mathbf{1});\ \Delta E_1 = -125.1\ \mathrm{kcal\,mol^{-1}} \quad (1)$$

$$(cAAC)_2Ni^{II}Cl_2\ (\mathbf{1}) + 2\ LiN\mathit{i}Pr_2 \rightarrow (cAAC)_2Ni\ (\mathbf{2}) + 2\ LiCl + Me_2CN\mathit{i}Pr + HN\mathit{i}Pr_2;\ \Delta E_2 = -12.8\ \mathrm{kcal\,mol^{-1}} \quad (2)$$

Reaction of **1** with $KN(SiMe_3)_2$ does not yield **2** because of the absence of an α-hydrogen atom. A plausible mechanism for the formation of **2** is given in the Supporting Information. Compound **2** is also obtained upon treating $(cAAC)_2Ni^{II}Cl_2$ (**1**) with KC_8 in a 1:2 molar ratio in THF. According to our synthetic strategy, we realized that reduction of **1** to **2** with LDA is superior to that with KC_8 because of the solubility of LDA in THF and its commercial availability.

Compound **2** has purple color in solution, whereas it appears as dark black shiny plates in the solid state. Compound **2** decomposes at 161 °C, while precursor **1** decomposes above 185 °C. Compound **2** is stable under an inert gas, although **1** is air-stable for 4 months. The black shiny plates of **2** are stable for 45 min upon exposure to air, but they then slowly lose their color and finally decompose into an unknown colorless solid. The UV/Vis spectrum of **2** in *n*-hexane shows absorption bands at 533, 611, and 807 nm (see the Supporting Information). The ^{13}C NMR spectrum of **2** exhibits a resonance at $\delta = 242.4$ ppm ($C_{carbene}$), which is upfield-shifted relative to the resonance of the free cAAC ($\delta = 304.2$ ppm).[9]

Compound **2** crystallizes from toluene as **2**·toluene in the triclinic space group $P\bar{1}$. The X-ray crystal structure of **2**·toluene shows two five-membered rings attached to one nickel atom. The nickel center is bound to each of the carbene carbon atoms and adopts an acyclic, bent, two-coordinate geometry (Figure 1).

The Ni–C and C–N bond lengths of **2** are 1.8448(14)/1.8419(13) and 1.3381(16)/1.3420(16) Å, respectively, which are comparable to those previously reported for $(NHC)_2Ni^{0}$.[5] $C_{NHC}{\rightarrow}Ni$ bond lengths are found in the range from 1.82 to 1.96 Å,[3–8] whereas those of $(NHC)Ni^{II}{=}N{-}R$[4a] and $(NHC)Ni^{I}(NHR)$[4b] with two-coordinate nickel atoms are 1.917(3) and 1.879(2) Å, respectively. The

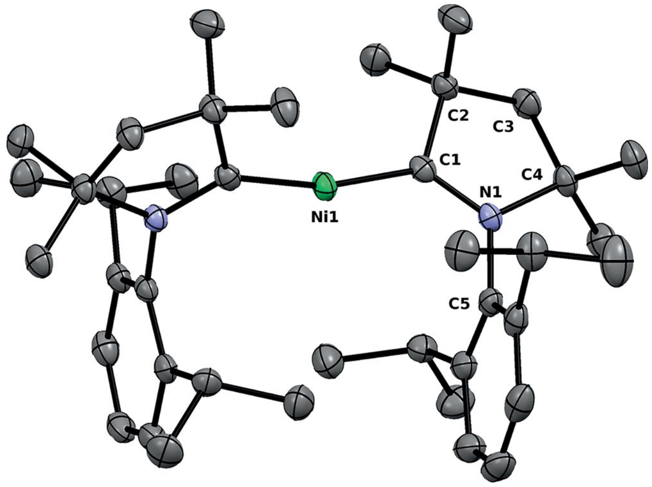


Figure 1. Molecular structure of compound **2** with thermal ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Selected [calculated at M06/def2-SVP singlet, triplet] bond lengths [Å] and angles [°]: Ni1–C1 1.8448(14) [1.846, 1.898], Ni1–C1_1 1.8419(13) [1.846, 1.898], C1–N1 1.3381(16) [1.340, 1.354], C1–N1_1 1.3420(16) [1.341, 1.352]; C1–Ni–C1_1 166.42(5) [165.6, 168.3], C2–C1–N1 106.49 (10) [106.4, 107.0], C2_1–C1_1–N1_1 106.40 (10) [106.4, 107.0].

Ni–C single bond lengths are 1.9150(14) and 1.9297(15) Å in the $(cAAC)_2Ni^{II}Cl_2$ (**1**) precursor. Shortening of the Ni–C bond and lengthening of the C–N bond (Supporting Information) in **2** is due to electronic backbonding from the nickel center to the carbene carbon atom. The C–Ni–C bond angle of **2** is 166.42°, which is 13° less than that of $(NHC)_2Ni^0$, also with two-coordinate nickel atom.[5] The angle between the two N–$C_{carbene}$–CMe_2 planes of **2** is 60.68°. The distance between the two carbene carbon atoms in **2** is 3.66 Å. The N–C–C–N torsion angle is 78° for **2**, whereas it is 180° for precursor **1**. The nickel atom of **2** also weakly interacts with the hydrogen atoms (2.90–3.00 Å) of the methyl groups of the carbene.

To obtain deeper insight into the electronic structure of **2**, theoretical calculations were performed within the DFT framework. Geometry optimizations were performed for the singlet closed-shell and triplet states at the M06/def2-SVP[11,12] level of theory. Selected bond lengths and angles are provided in the caption of Figure 1 (see Figures S7 and S8 for the superposition plots). The theoretical geometries indicate that the singlet state is in better agreement with the X-ray structure than the triplet species; the root-mean-square deviation values relative to the crystal structures are 0.127 Å for the former and 0.200 Å for the latter. We also checked the optimization of the open-shell species, but all attempts led to the singlet closed-shell species. The temperature dependence of the magnetic susceptibility (Supporting Information) confirms the singlet spin ground state of **2**.

Theoretical calculations at different levels predicted that the singlet closed-shell state lies below the triplet state by 18.7–34.9 $kcal\,mol^{-1}$ (Supporting Information).

The frontier molecular orbitals for the singlet closed-shell species are displayed in Figure S10. Clearly, the occupied frontier molecular orbitals are the d orbitals of the nickel atom, which in two cases has a small overlap with the p orbitals of the carbene carbon atoms on each ligand (HOMO–3 and HOMO–4). Interestingly, the LUMO is a π-type orbital on the $C_{carbene}$–Ni–$C_{carbene}$ bridge, which has a large contribution to the $C_{carbene}$ atoms and a small contribution to the Ni atom (Figure 2).

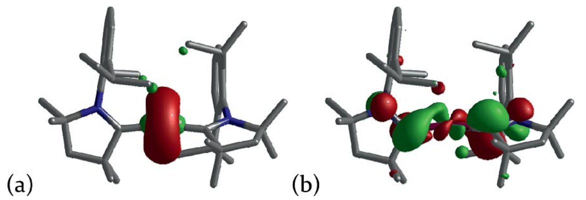


Figure 2. (a) HOMO and (b) LUMO of compound **2**.

Natural bond orbital (NBO)[13–16] analysis was performed to evaluate the natural charges over the $C_{carbene}$–Ni–$C_{carbene}$ bridge of **2**. The computed natural population analysis (NPA) charges on the carbene carbon atoms are 0.03 a.u., whereas the charge on the Ni atom is 0.34 a.u., which suggests the nature of this metal atom is between Ni^I and Ni^0. To confirm the contribution from the Ni^I character of $(cAAC)_2Ni$ (**2**), it was treated with the TEMPO (2,2,6,6-tetramethylpiperidine *N*-oxide) radical. (cAAC)-Ni^I–TEMPO was obtained as the product, which was characterized by ESI-MS [*m*/*z* (%) = 499.3(100)] (Supporting Information). For the sake of comparison between $(NHC)_2Ni^0$ and $(cAAC)_2Ni$ (**2**), we also optimized the structures of $(NHC)_2Ni^0$ (Supporting Information). The theoretical $C_{NHC}\rightarrow Ni$ bond lengths[5e] are 1.843 Å, which is in good agreement with the reported values.[5] For $(NHC)_2Ni^0$, NPA charges are 0.137 and –0.070 a.u. for the $C_{carbene}$ and Ni atoms, respectively, which is clearly suggestive of the Ni^0 nature. In contrast, the Wiberg bond order[17] of the Ni–$C_{carbene}$ bonds, for both complexes, is 0.74, as expected.

To obtain a more detailed picture, natural resonance theory (NRT)[18–20] analysis on **2** as a closed-shell species was performed. Particular focus on delocalization over $C_{carbene}$–Ni–$C_{carbene}$ was placed in our analysis. The resulting resonance structures (Scheme S5) indicate that there is a strong delocalization involving the N–$C_{carbene}$–Ni–$C_{carbene}$–N atoms, as a consequence of the π backdonation from the Ni d occupied orbitals to the empty $C_{carbene}$ p orbitals. Indeed, application of second-order perturbation theory within the NBO method revealed the occurrence of stabilizing two-electron delocalization from the sp^2 lone pairs of electrons of the carbene [LP($C_{carbene}$)] to the s orbital in nickel [LP*(Ni)] and from the d orbital of nickel [LP(Ni)] to the formally empty p orbitals on the carbene moiety [LP*($C_{carbene}$)]. The computed associated energies [$\Delta E^{(2)}$] are 135.0 and 59.8 $kcal\,mol^{-1}$ for LP($C_{carbene}$)→LP*(Ni) and LP(Ni)→LP*($C_{carbene}$), respectively. NBO also indicated a significant charge transfer from the occupied Ni d orbitals to the antibonding σ*(C–H) orbital on the isopropyl substituents (see structure description), which is a common interaction in complexes with low-valent metal oxidation states.[21–23]

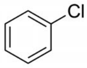
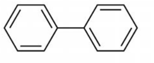
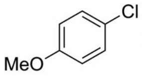
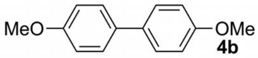
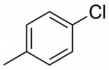
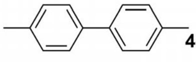
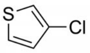
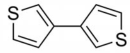
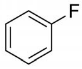
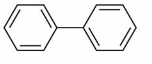
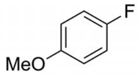
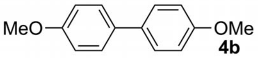
All ab initio calculations predicted the spin singlet to be the lowest in energy (Supporting Information).[24] We found that the Ni^0 electronic configuration is dominant in the ground singlet state. This result implies that compound **2** is a closed-shell singlet. Interestingly, the lowest and first excited spin triplets have one unpaired electron on Ni and another electron spanning one 2p orbital of the closest carbon atom (C1_1 in the structure file). Similar calculation on $(cAAC)_2Mn$ revealed that the ground state possesses Mn^I with a delocalized electron over two carbene carbon atoms.[25] To quantify the biradical character, we made use of the singlet biradical index proposed by Neese and coworkers (see the Supporting Information).[26]

Next, we intended to explore the catalytic reactivity of **2**. The homocoupling of aryl halides is one of the most powerful methods to form C–C bonds to give rise to an important class of compounds known as biaryls[27–29] and their heteroaromatic analogs. A stoichiometric amount of metallic Zn is used as the reducing agent in almost all Ni-catalyzed homocoupling reactions mainly involving aryl bromides or iodides as the self-coupling reagents. The use of readily available and inexpensive aryl chlorides is still scarce probably because of the high energy of the C–Cl bond. Catalytic activation of unactivated C–F bonds[1a] also remains a challenge till to date. In this context, nickel-catalyzed cross-coupling between unactivated aryl chlorides/fluorides and aryl Grignard reagents in the presence of different stabilizing ligands is noteworthy.[30,31]

Our initial investigations started with the use of 10 mol-% of **2** as the catalyst for the homocoupling of *para*-chlorotoluene (**3c**) in the presence of LDA as the reducing agent (Table S34). We obtained only a trace amount of the desired 4,4′-dimethylbiphenyl (**4c**) product after 24 h upon treating **3c** with 20 mol-% of LDA in THF at 65 °C. Increasing the amount of LDA to 1 equiv. (Table S34, Entry 2) also improved the product yield to 42%. Employing 2 equiv. of LDA successfully produced the desired product **4c** after 6 h in a good yield of 85% (Table S34, Entry 3). We next turned our attention to performing the reaction at ambient temperature, but unfortunately, we did not observe any reaction under this condition. Finally, we found 50 °C as the optimal temperature for our system, which gave rise to desired product **4c** in 84% yield after 6 h (Table S34, Entry 4). Reducing the catalyst loading to 5 and 2 mol-% led to a large decrease in the product yield (29% and 3%, respectively). For better functional-group tolerance, we screened weaker reducing agents, for example, potassium *tert*-butoxide (Table S34, Entry 6), but we obtained the biaryl in a much lower yield of 35% under the optimized reaction conditions. We also confirmed that no background reaction occurs in the absence of **2** (Table S34, Entry 7). Having the optimized reaction conditions in hand, we next explored the generality of the reaction; to our delight, we observed that not only the C–Cl bond but also the more unreactive C–F bond could activated by **2** to produce the desired biaryls in very good yields under relatively mild reaction conditions (Table 1). Utilization of CyMgCl (Cy = cyclohexyl) instead of LDA produced only a trace amount of the homocoupling product under the same reaction conditions (Table S34, Entry 5). For comparison, $(NHC)_2Ni$ {NHC=C[N(2,4-diisopropylphenyl)(CH)]$_2$} was also employed as a catalyst instead of $(cAAC)_2Ni$ (**2**). The yield of the reaction dropped to 10–12%, which suggests that **2** is a superior catalyst than the NHC analogue.

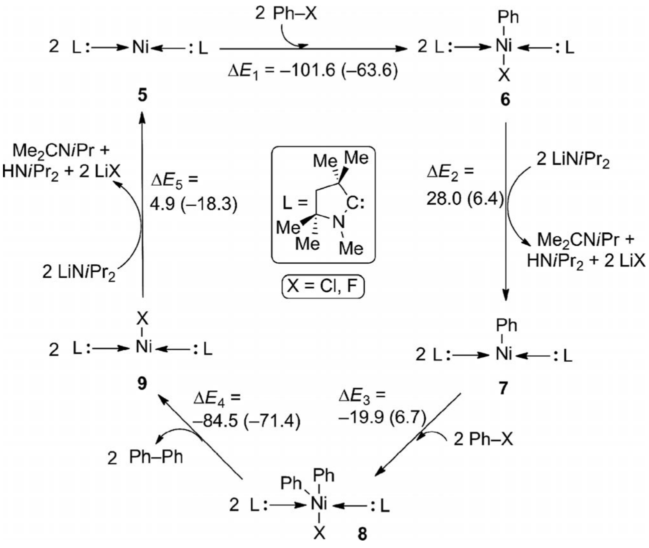
Table 1. Catalytic studies of compound **2**.[a]

$$\underset{\mathbf{3}}{2\ \mathrm{Ar{-}X}} \xrightarrow[\text{50 °C, 4–6 h}]{\text{Cat. }\mathbf{2}\text{ (10 mol-\%)}\\ \text{LDA, THF}} \underset{\mathbf{4}}{\mathrm{Ar{-}Ar}} \quad (\mathrm{X = Cl, F})$$

Entry	Aryl halide **3**	Product **4**	Yield [%][b]
1	 **3a**	 **4a**	78
2	 **3b**	 **4b**	91
3	 **3c**	 **4c**	84
4	 **3d**	 **4d**	85
5	 **3e**	 **4a**	55
6	 **3f**	 **4b**	62

[a] Reaction conditions: A mixture of **3** (2 mmol), catalyst **2** (0.1 mmol), and LDA (2 mmol) in dry THF (2 mL) was stirred under N_2 at 50 °C for 4–6 h. [b] Yield of isolated product after column chromatography.

A plausible reaction pathway is proposed, as shown in Scheme 2, on the basis of the energetics of the various steps involved and earlier experimental reports.[8] The first step of reaction can be considered as the activation of the Ph–X bond by oxidative addition to model catalyst **5**. The corresponding reaction energy (ΔE_1) for the formation of **6** by Ph–X (1 equiv.) is highly exothermic. This was also experimentally observed. Upon adding Ph–X, $(cAAC)_2Ni$ reacted vigorously, and heat was generated. This reaction process is more favorable for Ph–Cl [$\Delta E_{1(Cl)}$ = –50.8 kcal mol^{-1}] than for Ph–F [$\Delta E_{1(F)}$ = –31.8 kcal mol^{-1}], which can be correlated to the strength of the C–Cl and C–F bonds. The second step can be either dehalogenation of bisadduct **6** by LDA to give tricoordinate Ni^I complex **7** or further oxidative addition of a second molecule of Ph–X to give hexacoordinate Ni^{IV} complex **10** (Scheme S1). The latter process is highly endothermic (ΔE_{Cl} = 50.5 kcal mol^{-1} and ΔE_F = 44.7 kcal mol^{-1} for 1 equiv. of **6**) and hence can be excluded. However, the formation of tricoordinate complex **7** is only marginally endothermic by ΔE_2(Cl) = 14.0 kcal mol^{-1} and ΔE_2(F) = 3.2 kcal mol^{-1} for 1 equiv. of **6**. The formation of the Li–F bond, which is stronger than the Li–Cl bond, is reflected in the lower endothermicity for the defluorination process relative to that of the dechlorination reaction. Notably, the formation of tetracoordinate $(NHC)_2Ni^{II}(Ar)(Br)$ and tricoordinate $(NHC)_2Ni^{I}(Br)$ in the reaction of $(NHC)_2Ni^0$ and with an aryl bromide (ArBr) has been reported.[8] To form Ph–Ph, two phenyl groups should be in close proximity, and as a result, the oxidative addition of the second molecule of Ph–X to tricoordinate Ni^I intermediate **7** is proposed. The formation of corresponding pentacoordinate intermediate **8** by the oxidative addition of Ph–Cl is exothermic [$\Delta E_3(Cl) = -9.95$ kcal mol^{-1}], whereas that of Ph–F is slightly endothermic [$\Delta E_3(F) = 3.35$ kcal mol^{-1}] for 1 equiv. of **7**. Product formation through homocoupling of the two Ph groups is a highly favorable process [$\Delta E_4(Cl) = -42.25$ kcal mol^{-1} if X = Cl and $\Delta E_4(F) = -35.7$ kcal mol^{-1} if X = F for 1 equiv. of Ph–Ph].



Scheme 2. Schematic representation of the catalytic reaction of L_2Ni with Ph–X to give Ph–Ph. The reaction energy (ΔE in kcal mol^{-1}) for each step at the M06/def2-TZVPP//BP86/def2-SVP level of theory incorporating the zero-point energy correction from the BP86/def2-SVP level is also given. The values in parentheses are for X = F.

Ni^0 catalyst **5** can be regenerated from tricoordinate Ni^I intermediate **9** by reductive dehalogenation, which is marginally endothermic (2.45 kcal mol^{-1} per equivalent of **5**) for X = Cl and exothermic for X = F (-9.2 kcal mol^{-1} per equivalent of **5**), which can be attributed to the formation of the stronger Li–F bond. A similar oxidative addition product was proposed for various coupling reactions.[8] Thus, the overall catalytic reaction for both Ph–Cl and Ph–F is energetically favorable. The high exothermicity of the overall reaction supports the high yield obtained for the coupling reaction as well as the high reactivity of the cAAC as a ligand.

Conclusions

Utilizing the stronger complexation properties of a cAAC, $(cAAC)_2Ni^{II}Cl_2$ (**1**) was directly synthesized by treating cAAC with $NiCl_2$. Then, **1** was reduced to $(cAAC)_2Ni^0$ (**2**) by using LDA or KC_8 to provide direct access to a nickel(0) compound starting from nickel(II) dichloride and a carbene. On the basis of the calculated NBO charge values of the nickel atom for the $(NHC)_2Ni$ and $(cAAC)_2Ni$ (**2**) complexes, the oxidation state of nickel was found to be Ni^0 in $(NHC)_2Ni$ (–0.07) and between Ni^I and Ni^0 in **2** (+0.34). CASSCF(2,2)/def2-SVP//M06/def2-SVP calculations suggested a closed-shell singlet electronic configuration for **2** with little biradical character. Ab initio multiconfigurational C(R)ASSCF/CASPT2 calculations predicted a closed-shell singlet electronic configuration (Ni^0), whereas the excited spin states were predicted to possess Ni^I character with unpaired electrons on neighboring carbon atoms. The singlet ground state of **2** was confirmed by magnetic susceptibility measurements. The catalytic activity of complex **2** was investigated for the homocoupling of various unactivated aryl chlorides/fluorides. The biaryls were obtained in good yields at moderate temperature. A plausible reaction mechanism was proposed and supported by the favorable exothermic reaction energetics (Scheme 2).

Supporting Information (see footnote on the first page of this article): Experimental details.

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[1] a) E. Clot, O. Eisenstein, N. Jasim, S. A. Macgregor, J. E. McGrady, R. N. Perutz, *Acc. Chem. Res.* **2011**, *44*, 33–348; b) P. P. Power, *Chem. Rev.* **2012**, *112*, 3482–3507.

[2] a) R. E. Douthwaite, M. L. H. Green, P. J. Silcock, P. T. Gomes, *Organometallics* **2001**, *20*, 2611–2615; b) C. A. Laskowski, G. L. Hillhouse, *Organometallics* **2009**, *28*, 6114–6120.

[3] a) W. A. Herrmann, G. Gerstberger, M. Spiegler, *Organometallics* **1997**, *16*, 2209–2212; b) Z. Liu, Y.-C. Xu, L.-Z. Xie, H.-M. Sun, Q. Shen, Y. Zhang, *Dalton Trans.* **2011**, *40*, 4697–4706 and references cited therein; c) X. Wang, M. Sobota, F. T. U. Kohler, B. Morain, B. U. Melcher, M. Laurin, P. Wasserscheid, J. Libuda, K. Meyer, *J. Mater. Chem.* **2012**, *22*, 1893–1898.

[4] a) C. A. Laskowski, G. L. Hillhouse, *J. Am. Chem. Soc.* **2008**, *130*, 13846–13847; b) C. A. Laskowski, A. J. M. Miller, G. L. Hillhouse, T. R. Cundari, *J. Am. Chem. Soc.* **2011**, *133*, 771–773.

[5] a) A. J. Arduengo, S. F. Camper, J. C. Calabrese, F. Davidson, *J. Am. Chem. Soc.* **1994**, *116*, 4391–4394; b) S. Caddick, F. G. N. Cloke, P. B. Hitchcock, A. K. de K. Lewis, *Angew. Chem.* **2004**, *116*, 5948–5951; *Angew. Chem. Int. Ed.* **2004**, *43*, 5824–5827; c) K. Matsubara, S. Miyazaki, Y. Koga, Y. Nibu, T. Hashimura, T. Matsumoto, *Organometallics* **2008**, *27*, 6020–6024; d) A. A. Danopoulos, D. Pugh, *Dalton Trans.* **2008**, 30–31; e) U. Radius, F. M. Bickelhaupt, *Coord. Chem. Rev.* **2009**, *253*, 678–686; f) R. C. Poulten, M. J. Page, A. G. Algarra, J. J. Le Roy, I. Lopez, E. Carter, A. Llobet, S. A. Macgregor, M. F. Mahon, D. M. Murphy, M. Murugesu, M. K. Whittlesey, *J. Am. Chem. Soc.* **2013**, *135*, 13640–13643.

[6] a) T. Schaub, M. Backes, U. Radius, *Organometallics* **2006**, *25*, 4196–4206; b) C. H. Lee, D. S. Laitar, P. Mueller, J. P. Sadighi, *J. Am. Chem. Soc.* **2007**, *129*, 13802–13803.

[7] Y. Zhang, K. C. Ngeow, J. Y. Ying, *Org. Lett.* **2007**, *9*, 3495–3498.

[8] K. Zhang, M. Conda-Sheridan, S. R. Cooke, J. Louie, *Organometallics* **2011**, *30*, 2546–2552.

[9] a) V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2005**, *117*, 5851–5855; *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709; b) O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem.* **2013**, *125*, 3011–3015; *Angew. Chem. Int. Ed.* **2013**, *52*, 2939–2943.

[10] C. Kowalski, X. Creary, A. J. Rollin, M. C. Burke, *J. Org. Chem.* **1978**, *43*, 2601–2608.

[11] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.

[12] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[13] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.

[14] A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 1736–1740.

[15] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735–746.

[16] J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218.

[17] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083–1096.

[18] E. D. Glendening, J. K. Badenhoop, F. Weinhold, *J. Comput. Chem.* **1998**, *19*, 628–646.

[19] E. D. Glendening, F. Weinhold, *J. Comput. Chem.* **1998**, *19*, 593–609.

[20] E. D. Glendening, F. Weinhold, *J. Comput. Chem.* **1998**, *19*, 610–627.

[21] T. S. Thakur, G. R. Desiraju, *J. Mol. Struct.* **2007**, *810*, 143–154.

[22] M. Brookhart, M. L. H. Green, G. Parkin, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 6908–6914.

[23] E. S. Wiedner, J. Y. Yang, S. Chen, S. Raugei, W. G. Dougherty, W. S. Kassel, M. L. Helm, R. M. Bullock, M. R. DuBois, D. L. DuBois, *Organometallics* **2011**, *31*, 144–156.

[24] F. Aquilante, L. De Vico, N. Ferré, G. Ghigo, P. Malmqvist, P. Neogrády, T. B. Pedersen, M. Pitoňák, M. Reiher, B. O. Roos, L. Serrano-Andrés, M. Urban, V. Veryazov, R. Lindh, *J. Comput. Chem.* **2010**, *31*, 224–247.

[25] P. P. Samuel, K. C. Mondal, H. W. Roesky, M. Hermann, G. Frenking, S. Demeshko, F. Meyer, A. C. Stückl, J. H. Christian, N. S. Dalal, L. Ungur, L. F. Chibotaru, K. Pröpper, A. Meents, B. Dittrich, *Angew. Chem.* **2013**, *125*, 12033–12037; *Angew. Chem. Int. Ed.* **2013**, *52*, 11817–11821.

[26] a) V. Bachler, G. Olbrich, F. Neese, K. Wieghardt, *Inorg. Chem.* **2002**, *41*, 4179–4193; b) F. Neese, *J. Phys. Chem. Solids* **2004**, *65*, 781–785; c) D. Herebian, E. Bothe, F. Neese, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.* **2003**, *125*, 9116–9128; d) D. Herebian, K. E. Wieghardt, F. Neese, *J. Am. Chem. Soc.* **2003**, *125*, 10997–11005; e) E. Miliordos, K. Ruedenberg, S. S. Xantheas, *Angew. Chem.* **2013**, *125*, 5848–5851; *Angew. Chem. Int. Ed.* **2013**, *52*, 5736–5739.

[27] R. C. Larock, *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*, 2nd ed., Wiley-VCH, Weinheim, **1999**.

[28] a) P. E. Fanta, *Chem. Rev.* **1964**, *64*, 613–632; b) P. E. Fanta, *Synthesis* **1974**, 9–21.

[29] J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359–1470.

[30] a) T. Takahashi, K. Kanno, *Modern Organonickel Chemistry* (Ed.: Y. Tamaru), Wiley-VCH, Weinheim, **2005**, pp. 41–55; b) H. Amii, K. Uneyama, *Chem. Rev.* **2009**, *109*, 2119–2183.

[31] L. Ackermann, R. Born, J. H. Spatz, D. Meyer, *Angew. Chem.* **2005**, *117*, 7382–7386; *Angew. Chem. Int. Ed.* **2005**, *44*, 7216–7219.

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Carbene Ligands

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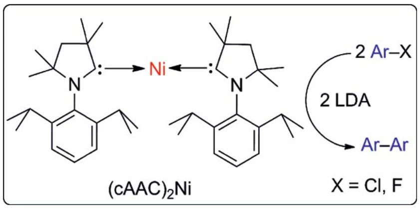

The synthesis of (cAAC)$_2$Ni^{II}Cl$_2$ (**1**) and its conversion into (cAAC)$_2$Ni (**2**) through reduction is reported [cAAC = cyclic (alkyl)-(amino)carbene]. Efficient reductive homocoupling of unactivated aryl chlorides and fluorides is catalyzed by **2** through C–Cl and C–F bond activation. Detailed high-level theoretical investigations are performed to understand the electronic and catalytic cycle of **2**.