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Nickel(II) complexes with novel nitron-type NHC ligands: synthesis and catalytic activity in the Suzuki–Miyaura coupling of aryl chlorides

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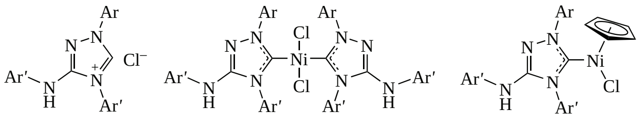
A new method has been developed for synthesizing nitron-type 1,4-dyaryl-3-arylamino-1,2,4-triazolium salts through a stepwise reaction of *N,N′*-diarylcarbodiimides with aryl hydrazines, trimethyl orthoformate and Me$_3$SiCl. These salts have been utilized as NHC-proligands to prepare novel (NHC)$_2$NiCl$_2$ and (NHC)NiCpCl (Cp = cyclopentadienyl anion) complexes. Catalytic trials of these complexes uncovered a highly effective catalyst for the Suzuki–Miyaura cross-coupling of non-activated aryl chlorides.



Keywords: N-heterocyclic carbene, nickel complexes, Nitron, catalysis, aryl chlorides, Suzuki–Miyaura coupling.

N-Heterocyclic carbenes (NHCs) have been widely used as strong sigma-donating ligands in metal catalysis.[1–4] During the past decade, NHC ligands bearing negatively charged groups or acquiring negative charge under certain reaction conditions have attracted much attention [Figure 1(*a*)].[5–8] Anionic substituents in the backbone of aromatic NHCs can significantly enhance the electron density donation from the NHC to a metal center.[5] Nitron, a common analytical reagent for the gravimetric determination of nitrate ion [Figure 1(*b*)],[9] and similar nitron-type 1,2,4-triazole derivatives, can be used as NHC ligands capable of acquiring anionic character *via* NH deprotonation in basic medium [Figure 1(*c*)].[10–18] Recent studies have demonstrated that the ionization of nitron-type ligands in the presence of bases provided a substantial stabilizing effect on the metal–NHC bond in Pd/NHC complexes, and retarded their decomposition in alkaline medium.[15] Although various nitron-type compounds with simple *N*-aryl[19–23] or *N*-alkyl[12,15,16,24] substituents have been reported, nitron-type ligands containing bulky *N*-aryl groups such as Mes (2,4,6-trimethylphenyl) or DiPP (2,6-diisopropylphenyl), which are commonly used in M/NHC catalysis, have yet to be explored.

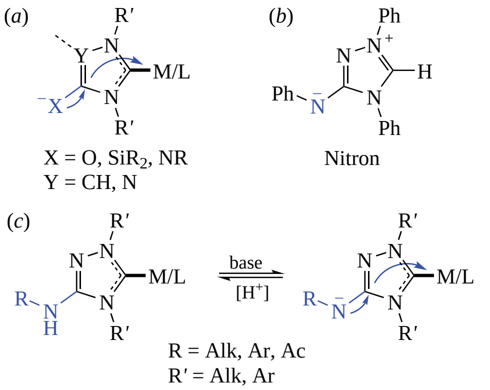
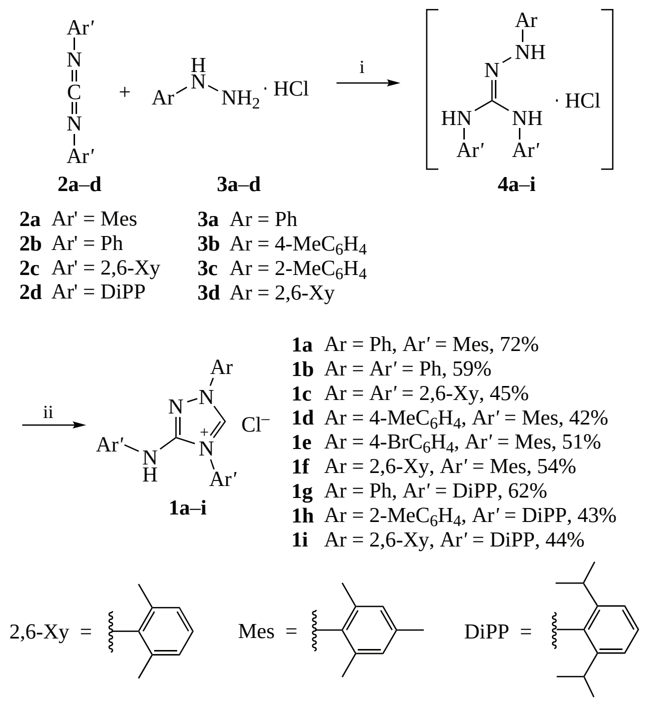


Figure 1 (*a*) Representative structures of metal complexes with NHC ligands containing anionic substituents; (*b*) Nitron and (*c*) ionization of M/NHC complexes with nitron-type NHC-ligands in the basic medium.

Herein, we report an efficient method for the preparation of 1,4-diaryl-3-arylamino-1,2,4-triazolium salts with various *N*-aryl groups, including Mes and DiPP, and the synthesis of new Ni/NHC complexes using the obtained nitron-type salts as NHC proligands. Notably, several of the synthesized Ni complexes were found to be highly efficient in catalyzing the Suzuki–Miyaura reaction between aryl chlorides and arylboronic acids.

The synthesis of new nitron-type 1,4-diaryl-3-arylamino-1,2,4-triazolium salts **1a**–**i** was achieved through a two-step process (Scheme 1). The first step, the reaction of *N,N′*-diarylcarbodiimides **2** with arylhydrazine hydrochlorides **3** to afford triarylaminoguanidines **4**, was carried out similarly to the previously reported procedure for the preparation of amidrazones from imidoyl chlorides and arylhydrazine hydrochlorides.[25] In the second step, crude triarylaminoguanidines **4** were reacted with cyclizing agents to give compounds **1a**–**i**. The conditions of the second step were optimized on an example of the synthesis of compound **1a** (see Online Supplementary Materials, Table S1). Attempts to use formic acid under reflux or formaldehyde with subsequent oxidation of the condensation products[23] were unsuccessful (see Table S1, entries 1 and 2). However, the use of trimethyl orthoformate and anhydrous HCl (in dioxane) or, preferentially, Me$_3$SiCl, the well-known promoter of various heterocyclizations in 1,2,4-triazole chemistry,[26,27] resulted in the formation of the desired compound **1a** (entries 6–14). The conditions shown in Scheme 1 were accepted as optimal. Using the optimized conditions, we synthesized the nitron-type salts **1a**–**i** in 42–72% isolated yields (see Scheme 1).

Salts **1a**–**i** were investigated as potential nitron-type NHC proligands for the synthesis of Ni/NHC complexes. Heating



2a–d **3a–d** **4a–i**

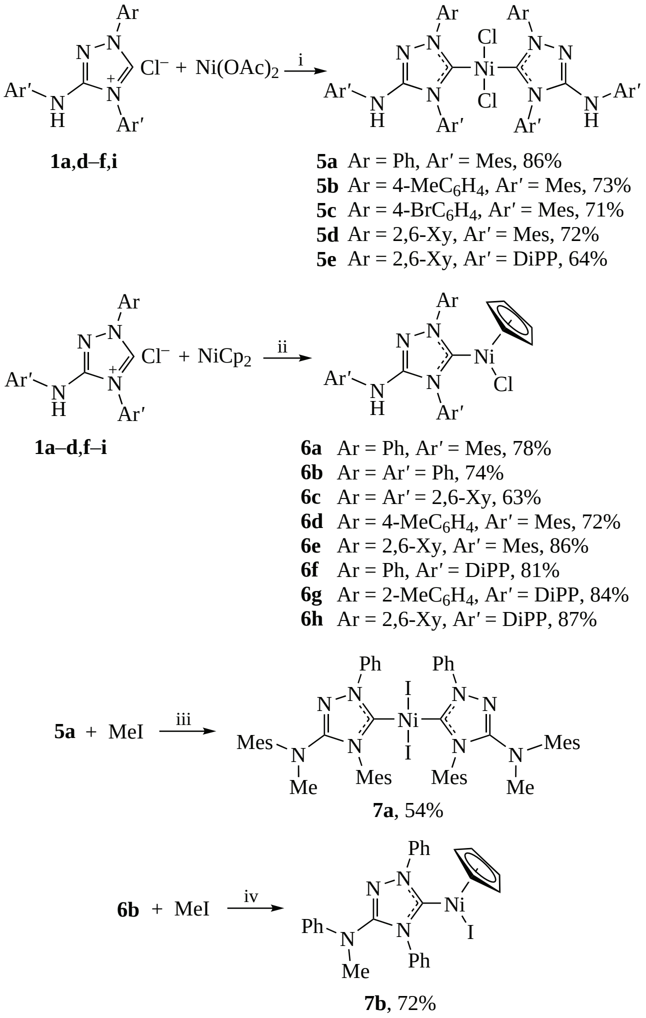
2a Ar′ = Mes
2b Ar′ = Ph
2c Ar′ = 2,6-Xy
2d Ar′ = DiPP

3a Ar = Ph
3b Ar = 4-MeC_6H_4
3c Ar = 2-MeC_6H_4
3d Ar = 2,6-Xy

1a–i

1a Ar = Ph, Ar′ = Mes, 72%
1b Ar = Ar′ = Ph, 59%
1c Ar = Ar′ = 2,6-Xy, 45%
1d Ar = 4-MeC_6H_4, Ar′ = Mes, 42%
1e Ar = 4-BrC_6H_4, Ar′ = Mes, 51%
1f Ar = 2,6-Xy, Ar′ = Mes, 54%
1g Ar = Ph, Ar′ = DiPP, 62%
1h Ar = 2-MeC_6H_4, Ar′ = DiPP, 43%
1i Ar = 2,6-Xy, Ar′ = DiPP, 44%

Scheme 1 *Reagents and conditions*: i, **2a–d** (3.88 mmol), **3a–d** (4 mmol), Et_3N (7.8 mmol), THF (15 ml), room temperature, 16 h; ii, $HC(OMe)_3$ (12.8 mmol), Me_3SiCl (8.54 mmol), EtOAc (7 ml), 80 °C, 3 h.



1a,**d**–**f**,**i**

5a Ar = Ph, Ar′ = Mes, 86%
5b Ar = 4-MeC_6H_4, Ar′ = Mes, 73%
5c Ar = 4-BrC_6H_4, Ar′ = Mes, 71%
5d Ar = 2,6-Xy, Ar′ = Mes, 72%
5e Ar = 2,6-Xy, Ar′ = DiPP, 64%

1a–**d**,**f**–**i**

6a Ar = Ph, Ar′ = Mes, 78%
6b Ar = Ar′ = Ph, 74%
6c Ar = Ar′ = 2,6-Xy, 63%
6d Ar = 4-MeC_6H_4, Ar′ = Mes, 72%
6e Ar = 2,6-Xy, Ar′ = Mes, 86%
6f Ar = Ph, Ar′ = DiPP, 81%
6g Ar = 2-MeC_6H_4, Ar′ = DiPP, 84%
6h Ar = 2,6-Xy, Ar′ = DiPP, 87%

7a, 54%

7b, 72%

Scheme 2 *Reagents and conditions*: i, azolium salt **1a**,**d**–**f**,**i** (0.1 mmol), $Ni(OAc)_2$ (0.05 mmol), 1,4-dioxane (2 ml), 110 °C, 2 h; ii, azolium salt **1a**–**d**,**f**–**i** (0.5 mmol), $NiCp_2$ (0.75 mmol), THF (5 ml), 60 °C 3 h; iii, complex **5a** (0.1 mmol), MeI (0.26 mmol), K_3PO_4 (0.4 mmol), KI (1 mmol), MeCN (2 ml), room temperature, 12 h; iv, complex **6b** (0.1 mmol), MeI (0.26 mmol), Bu^tOK (0.12 mmol), KI (1 mmol), THF (2 ml), room temperature, 12 h.

compounds **1a**,**d**–**f**,**i** with $Ni(OAc)_2$ in 1,4-dioxane at 110 °C, similarly to the recently described procedure for the synthesis of bis-NHC nickel complexes,[28] led to compounds **5a**–**e** in 64–86% yields (Scheme 2). Compounds **1a**–**d**,**f**–**i** reacted smoothly with nickelocene in THF to afford (NHC)Ni(Cp)Cl complexes **6a**–**h** in 63–87% yields. Pink colored complexes **5** and dark red complexes **6** were isolated as air stable crystalline compounds soluble in most common organic solvents. It should be noted that dissolved complexes **5** and **6** decomposed within a few hours in the presence of water in organic solvents. Gradual discoloration and precipitation of nickel hydroxide was observed after the addition of several drops of water to the solutions of complexes **5** and **6** in THF, dioxane or MeCN. Instability of various Ni/NHC complexes in the presence of water has been reported in the literature.[29]

The possibility of ionization of nitron-type ligands in the synthesized Ni/NHC complexes in the presence of bases [see Figure 1(*c*)] was confirmed by selective *N*-alkylation of complexes **5a** and **6b** with iodomethane in the presence of K_3PO_4 or Bu^tOK to give complexes **7a** and **7b**, respectively (see Scheme 2). Only the initial complexes **5a** and **6b** were recovered when alkylation was attempted in the absence of bases. Therefore, the formation of complexes **7a** and **7b** can only occur through the intermediate formation of deprotonated forms of **5a** and **6b** [see Figure 1(*c*)].

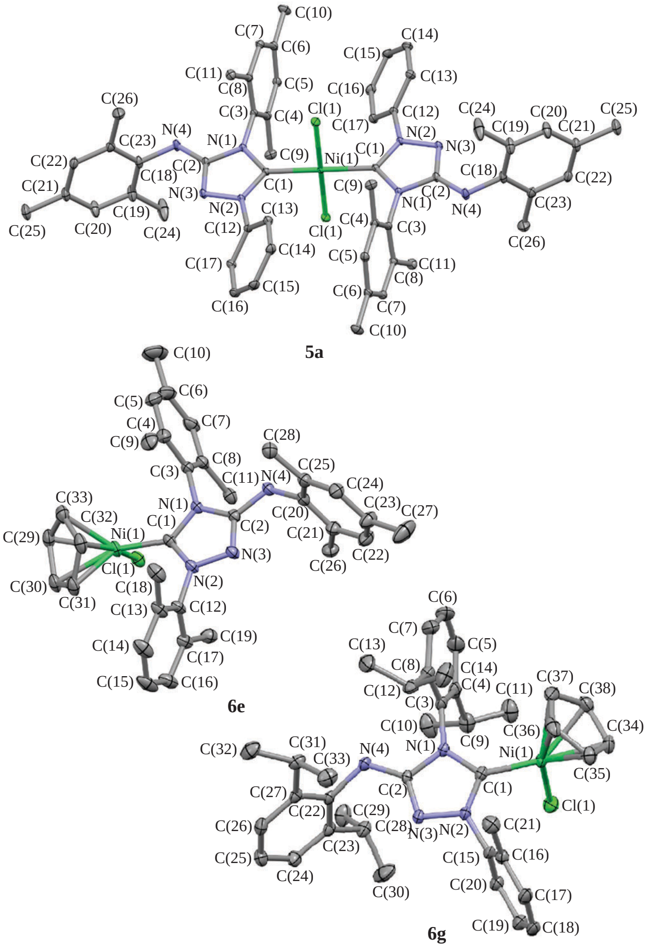
Structures of compounds **1a**–**i**, **5a**–**e**, **6a**–**h** and **7a**,**b** were confirmed by ^1H and ^{13}C NMR spectra, elemental analyses and single crystal X-ray study of complexes **5a**, **6e** and **6g** (Figure 2).[†]

[†] *Crystal data for* **5a** (two radiation wavelengths were used). $C_{52}H_{56}Cl_2N_8Ni\cdot 2(CH_2Cl_2)$, $M_r = 1092.51$, monoclinic, $P2_1/c$ at 100.0(1) K, $\lambda = 0.71073$ Å, $a = 16.3057(3)$, $b = 14.41195(19)$ and $c = 1.8836(2)$ Å, $\beta = 110.635(2)°$, $V = 2613.45(8)$ Å^3, $Z = 2$, $d_{calc} = 1.388$ g cm^{-3}, $\mu(MoK\alpha) = 0.72$ mm^{-1}, $F(000) = 1140$. Total of 47987 reflections were measured and 10193 independent reflections ($R_{int} = 0.025$) were used. The refinement converged to $wR_2 = 0.0854$ and GOF = 1.06 for all independent reflections [$R_1 = 0.0311$ was calculated against F for 8944 observed reflections with $I > 2\sigma(I)$]. $\lambda = 1.54184$ Å, $a = 16.30763(10)$, $b = 14.41133(6)$ and $c = 11.87970(7)$ Å, $\beta = 110.6127(7)°$, $V = 2613.17(3)$ Å^3, $Z = 2$, $d_{calc} = 1.388$ g cm^{-3}, $\mu(CuK\alpha) = 3.71$ mm^{-1}, $F(000) = 1140$. Total of 44665 reflections were measured and 5695 independent reflections ($R_{int} = 0.025$) were used. The refinement converged to $wR_2 = 0.0791$ and GOF = 1.04 for all independent reflections [$R_1 = 0.0295$ was calculated against F for 5579 observed reflections with $I > 2\sigma(I)$].

Crystal data for **6e**. $C_{33}H_{37}ClN_4Ni$, $M_r = 583.82$, orthorhombic, *Pbcn* at 100.0(1) K, $a = 20.10910(10)$, $b = 18.39695(8)$ and $c = 18.19766(8)$ Å, $V = 6732.15(5)$ Å^3, $Z = 8$, $d_{calc} = 1.152$ g cm^{-3}, $\mu(CuK\alpha) = 1.75$ mm^{-1}, $F(000) = 2464$. Total of 55294 reflections were measured and 7325 independent reflections ($R_{int} = 0.024$) were used. The refinement converged to $wR_2 = 0.0798$ and GOF = 1.03 for all independent reflections [$R_1 = 0.0277$ was calculated against F for 6974 observed reflections with $I > 2\sigma(I)$]. A highly disordered non-coordinating molecule was removed by the Solvent Mask procedure.

Crystal data for **6g**. $C_{38}H_{47}ClN_4Ni\cdot H_2O$, $M_r = 671.97$, orthorhombic, $P2_12_12_1$ at 100.0(1) K, $a = 10.01462(8)$, $b = 17.91785(15)$ and $c = 19.61513(15)$ Å, $V = 3519.75(5)$ Å^3, $Z = 4$, $d_{calc} = 1.268$ g cm^{-3}, $\mu(CuK\alpha) = 1.76$ mm^{-1}, $F(000) = 1432$. Total of 50676 reflections were measured and 7677 independent reflections ($R_{int} = 0.042$) were used. The refinement converged to $wR_2 = 0.0719$ and GOF = 1.08 for all independent reflections [$R_1 = 0.0296$ was calculated against F for 7622 observed reflections with $I > 2\sigma(I)$].

CCDC 2301724, 2301725, 2301726 and 2301727 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.



5a

6e

6g

Figure 2 X-ray structure of compounds **5a**, **6e** and **6g**, p = 50%. Hydrogen atoms are not shown for clarity.

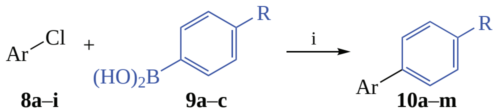
NMR spectra of compounds **1a**–**i** are similar to those of other nitron-type triazolium salts,[15] whereas NMR spectra of complexes **5a**–**e** and **6a**–**h** are analogous to the spectra of $(NHC)_2NiX_2$ (X = Cl, Br, I),[28–30] and (NHC)Ni(Cp)X[16] complexes reported in the literature. In the ^{1}H NMR spectra of complexes **5a**–**e** and **6a**–**h**, broadened NH signal at 4.7–6.8 ppm (in compounds **5**) and 5.0–6.0 ppm (in compounds **6**) is detected, it disappears upon deuteration. The ^{1}H NMR spectra of compounds **6a**–**h** also demonstrate characteristic singlet for the η-coordinated Cp ligand at 4.6–4.7 ppm.[16] In the ^{1}H NMR spectra of compounds **5** and **6**, splitting of NH signals, apparently due to hindered rotation of bulky Ar groups, is observed.[16,28] Structures of complexes **7a**,**b** were also confirmed by ^{1}H–^{13}C HMBC spectra (Figures S50 and S53) which contain correlation peaks between the protons for NMe groups (2.97 ppm for **7a**, 3.28 ppm for **7b**) and neighboring atom C of triazole ring (159.9 ppm for **7a**, 157.0 ppm for **7b**) as well as with the C_{ipso} of *N*-aryl group (138.4 ppm for **7a**, 145.2 ppm for **7b**).

The molecular geometry of compound **5a** (see Figure 2) is similar to those of the previously described $(NHC)_2NiX_2$ complexes.[24,28,30] The molecule adopts square-planar geometry with mutually *trans* positions of both NHC ligands and Cl ligands. The C−Ni−C and Cl−Ni−Cl bond angles are 180.0°, a small scissoring distortion is observed so that the C−Ni−Cl angles of 91.1(3)° and 88.9(3)° are slightly different from 90°. The molecular geometries of compounds **6e** and **6g** are similar to those described for (NHC)Ni(Cp)X complexes with nitron-type[16] and imidazole-type ligands.[31]

Table 1 Catalytic activity of Ni/NHC complexes in the SM reaction between **8a** and **9a**.[a]

Entry	[Ni]	Yield of **10a** (%)[b]
1	**5a**	85
2	**5b**	81
3	**5c**	80
4	**5d**	66
5	**5e**	22
6	**6a**	19
7	**6b**	13
8	**6c**	12
9	**6d**	17
10	**6e**	15
11	**6f**	9
12	**6g**	10
13	**6h**	11
14	**7a**	74
15	**7b**	11
16	**11a**	63
17	**11b**	20
18	**12a**	10
19	**12b**	9

[a] *Reagents and conditions*: **8a** (0.1 mmol), **9a** (0.15 mmol), K_3PO_4 (0.3 mmol), [Ni] (0.5 mol%), dioxane (0.5 ml), 90 °C, reaction time 5 h. [b] The yield was determined by GC-MS.



8a–i **9a–c** **10a–m**

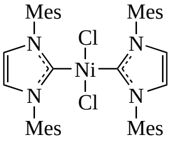
8a Ar = 3-MeC$_6$H$_4$
8b Ar = 2-MeC$_6$H$_4$
8c Ar = 4-MeC$_6$H$_4$
8d Ar = 4-FC$_6$H$_4$
8e Ar = 4-F$_3$CC$_6$H$_4$
8f Ar = 4-NCC$_6$H$_4$
8g Ar = 4-MeC(O)C$_6$H$_4$
8h Ar = 4-MeOC$_6$H$_4$
8i Ar = 2-MeOC$_6$H$_4$

9a R = H
9b R = MeO
9c R = CF$_3$

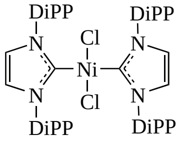
10a Ar = 3-MeC$_6$H$_4$, R = H, 79%
10b Ar = 2-MeC$_6$H$_4$, R = H, 86%
10c Ar = 4-MeC$_6$H$_4$, R = H, 88%
10d Ar = 4-FC$_6$H$_4$, R = H, 94%
10e Ar = 4-F$_3$CC$_6$H$_4$, R = H, 92%
10f Ar = 4-NCC$_6$H$_4$, R = H, 73%
10g Ar = 4-MeC(O)C$_6$H$_4$, R = H, 92%
10h Ar = 4-MeOC$_6$H$_4$, R = H, 78%
10i Ar = 4-MeOC$_6$H$_4$, R = MeO, 68%
10j Ar = 4-MeOC$_6$H$_4$, R = CF$_3$, 54%
10k Ar = 2-MeOC$_6$H$_4$, R = H, 66%
10l Ar = 2-MeOC$_6$H$_4$, R = MeO, 81%
10m Ar = 2-MeOC$_6$H$_4$, R = CF$_3$, 68%

Scheme 3 *Reagents and conditions*: i, **8a**–**i** (0.5 mmol), **9a**–**c** (0.7 mmol), K_3PO_4 (318 mg, 1.5 mmol), **5a** (0.5 mol%), dioxane (2.5 ml), 90 °C, 5 h. Isolated yields of **10a**–**m** are presented.

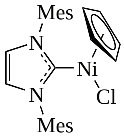
Complexes **5a**–**e**, **6a**–**h** and **7a**,**b** were investigated as potential precatalysts of the Suzuki–Miyaura (SM) cross-coupling between compounds **8a** and **9a** to give **10a** under conditions reported previously for Ni/NHC catalyzed SM reaction (Table 1, Scheme 3).[32,33] Complexes **11a**,**b**[28] and **12a**,**b**[31] widely used in catalysis were also tested for comparison. Bis-NHC nickel complexes **5a**–**e** and **11a**,**b** exhibited higher activity (see Table 1, entries 1–5, 16, 17) than (NHC)Ni(Cp)Cl complexes **6a**–**h** and **12a**,**b** under the conditions studied (entries 6–13, 18, 19). It is interesting to note that complexes **5d**,**e** and **11b** with bulkier NHC ligands were less active than complexes **5a** and **11a**. Complex **5a** was found to be the most efficient precatalyst, surpassing the efficiency of all other Ni/NHC complexes studied, including complexes **11** and **12** (compare entries 1 and 16–19). We also investigated variation of reaction conditions in terms of solvent, base, catalyst loading and reaction time, but no significant improvement in **10a** yield was achieved (Table S2).



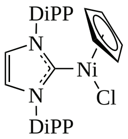
11a



11b



12a



12b

The high catalytic efficiency of complex **5a** was also demonstrated in the synthesis of a series of biaryls **10a**–**m** from aryl chlorides **8a**–**i** and arylboronic acids **9a**–**c** (see Scheme 3). Remarkably, complex **5a** showed high catalytic performance at loadings as low as 0.5 mol% in the reactions of aryl chlorides **8b**,**c**,**h**,**i** containing electron donating groups and *ortho* substituents, which are usually reluctant coupling partners.[34,35] Although Ni/NHC catalytic systems operating at lower Ni loadings (0.2–0.25 mol%) have been reported previously, these systems required the use of phosphine ligand additives to achieve high performance in the reactions of unactivated aryl chlorides.[36,37] To the best of our knowledge,[34,35] complex **5a** may be related to the most efficient Ni/NHC precatalysts for the SM reaction of unactivated aryl chlorides.

The mechanism of catalysis by complex **5a** necessitates separate in-depth investigation. Nevertheless, it is possible to suggest that the deprotonated form of complex **5a** containing the anionic NHC ligand [see Figure 1(*c*)] can be involved in the catalytic cycle. The assumption of the participation of the anionic forms of **5a** in the catalysis under the studied conditions is consistent with the results of the experiment on the *N*-alkylation of complex **5a** in the presence of K_3PO_4 as a base (see Scheme 2).

In conclusion, a novel method for the synthesis of nitron-type 1,4-diaryl-3-arylamino-1,2,4-triazolium salts by stepwise reaction of *N*,*N'*-diarylcarbodiimides with aryl hydrazines, trimethyl orthoformate and Me_3SiCl has been developed. The synthesized nitron-type salts have been proved to serve as NHC proligands by the synthesis of novel $(NHC)_2NiCl_2$ and (NHC)Ni(Cp)Cl complexes. Special alkylation experiments showed that NHC ligands of these complexes could be ionized by NH deprotonation in the presence of K_3PO_4 or potassium *tert*-butoxide. Catalytic activity studies of the synthesized Ni/NHC complexes uncovered a highly efficient precatalyst for the Suzuki–Miyaura reaction, complex **5a**, which facilitates cross-coupling of inactivated aryl chlorides at 0.5 mol% loading without phosphine additives.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.01.012.

References

1 S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612.
2 P. Bellotti, M. Koy, M. N. Hopkinson and F. Glorius, *Nat. Rev. Chem.*, 2021, **5**, 711.
3 K. Matsubara, *Chem. Rec.*, 2021, **21**, 3925.
4 V. M. Chernyshev, E. A. Denisova, D. B. Eremin and V. P. Ananikov, *Chem. Sci.*, 2020, **11**, 6957.
5 A. Nasr, A. Winkler and M. Tamm, *Coord. Chem. Rev.*, 2016, **316**, 68.
6 E. Peris, *Chem. Rev.*, 2018, **118**, 9988.
7 D. Munz and K. Meyer, *Nat. Rev. Chem.*, 2021, **5**, 422.
8 L. P. Ho and M. Tamm, *Chem. – Eur. J.*, 2022, **28**, e202200530.
9 C. Färber, M. Leibold, C. Bruhn, M. Maurer and U. Siemeling, *Chem. Commun.*, 2012, **48**, 227.
10 S. Hitzel, C. Färber, C. Bruhn and U. Siemeling, *Organometallics*, 2014, **33**, 425.
11 C. Thie, S. Hitzel, L. Wallbaum, C. Bruhn and U. Siemeling, *J. Organomet. Chem.*, 2016, **821**, 112.
12 C. Thie, C. Bruhn, M. Leibold and U. Siemeling, *Molecules*, 2017, **22**, 1133.
13 M. Sevim, S. B. Kavukcu, A. Kınal, O. Şahin and H. Türkmen, *Dalton Trans.*, 2020, **49**, 16903.
14 E. Amit, I. Berg and E. Gross, *Chem.– Eur. J.*, 2020, **26**, 13046.
15 A. Yu. Chernenko, A. V. Astakhov, V. V. Kutyrev, E. G. Gordeev, J. V. Burykina, M. E. Minyaev, V. N. Khrustalev, V. M. Chernyshev and V. P. Ananikov, *Inorg. Chem. Front.*, 2021, **8**, 3382.
16 V. V. Chesnokov, M. A. Shevchenko, S. B. Soliev, V. A. Tafeenko and V. M. Chernyshev, *Russ. Chem. Bull.*, 2021, **70**, 1281.
17 D. V. Pasyukov, A. Y. Chernenko, K. E. Shepelenko, V. V. Kutyrev, V. N. Khrustalev and V. M. Chernyshev, *Mendeleev Commun.*, 2021, **31**, 176.
18 M.-Y. Lee, C.-H. Liao, H.-Y. Hung, J.-Y. Lee and H. M. Lee, *RSC Adv.*, 2023, **13**, 27434.
19 M. Busch, *Ber. Dtsch. Chem. Ges.*, 1905, **38**, 856.
20 M. Busch and G. Mehrtens, *Ber. Dtsch. Chem. Ges.*, 1905, **38**, 4049.
21 M. Busch, *J. Prakt. Chem.*, 1906, **74**, 533.
22 E. Gehrer, W. Harder, K. Ebel, J.-P. Melder and J. H. Teles, *Patent US 5298668*, 1994.
23 A. Kriven’ko and N. Morozova, *Russ. J. Appl. Chem.*, 2006, **79**, 506 (*Zh. Prikl. Khim.*, 2006, **79**, 515).
24 V. M. Chernyshev, A. G. Vlasova, A. V. Astakhov, S. V. Shishkina and O. V. Shishkin, *J. Org. Chem.*, 2015, **80**, 375.
25 V. R. Yatham, W. Harnying, D. Kootz, J.-M. Neudörfl, N. E. Schlörer and A. Berkessel, *J. Am. Chem. Soc.*, 2016, **138**, 2670.
26 A. V. Astakhov, K. Yu. Suponitsky and V. M. Chernyshev, *Mendeleev Commun.*, 2018, **28**, 439.
27 S.-E. Tsai, S.-M. Li, C.-C. Tseng, C.-Y. Chung, Y.-H. Zeng, C. C. Lin, M.-T. Fuh, L.-C. Yang, Y.-C. Yang and F.-F. Wong, *Bioorg. Chem.*, 2020, **104**, 104299.
28 O. V. Khazipov, A. S. Pyatachenko, D. V. Pasyukov, M. E. Minyaev and V. M. Chernyshev, *Mendeleev Commun.*, 2023, **33**, 180.
29 A. V. Astakhov, O. V. Khazipov, E. S. Degtyareva, V. N. Khrustalev, V. M. Chernyshev and V. P. Ananikov, *Organometallics*, 2015, **34**, 5759.
30 P. J. Quinlivan, A. Loo, D. G. Shlian, J. Martinez and G. Parkin, *Organometallics*, 2021, **40**, 166.
31 R. A. Kelly, N. M. Scott, S. Díez-González, E. D. Stevens and S. P. Nolan, *Organometallics*, 2005, **24**, 3442.
32 T. Tu, H. Mao, C. Herbert, M. Xu and K. H. Dötz, *Chem. Commun.*, 2010, **46**, 7796.
33 S. Wang, F. Ren, Y. Qiu and M. Luo, *J. Organomet. Chem.*, 2015, **788**, 27.
34 F.-S. Han, *Chem. Soc. Rev.*, 2013, **42**, 5270.
35 I. P. Beletskaya, F. Alonso and V. Tyurin, *Coord. Chem. Rev.*, 2019, **385**, 137.
36 Y. Zhou, Z. Xi, W. Chen and D. Wang, *Organometallics*, 2008, **27**, 5911.
37 S. Ando, H. Matsunaga and T. Ishizuka, *J. Org. Chem.*, 2017, **82**, 1266.

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