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Mendeleev Commun., 2024, **34**, 822–824

Mendeleev Communications

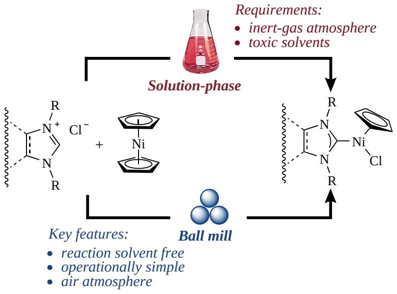
A novel mechanochemical synthesis of cyclopentadienyl-type Ni/NHC complexes

Oleg V. Khazipov,* Anastasia S. Pyatachenko and Victor M. Chernyshev

Platov South-Russian State Polytechnic University, 346428 Novocherkassk, Russian Federation.
E-mail: hazipov@bk.ru, chern13@yandex.ru

DOI: 10.1016/j.mencom.2024.10.017

A user-friendly and highly efficient mechanochemical synthesis of Ni/NHC complexes of the general formula (NHC)Ni(Cp)Cl (NHC is an N-heterocyclic carbene ligand; Cp is the cyclopentadienyl anion) under aerobic conditions is reported. The reaction between nickelocene and azolium salts (NHC proligands) proceeds with good to excellent yields of (NHC)Ni(Cp)Cl in the presence of a K_2CO_3 additive, which reduces the clumping of the reaction mixture. The developed process can be scaled up on a planetary ball mill.



Keywords: nickel complexes, azolium salts, N-heterocyclic carbene, ligands, mechanochemical synthesis, ball milling.

Nickel complexes are widely used in cross-coupling, C–H bond functionalization and many other reactions that play an important role in contemporary organic synthesis.[1–3] Among the many of well-defined nickel complexes, species that bear N-heterocyclic carbene (NHC) ligands play indisputably a prominent role in catalysis.[4–6] Advantages of NHCs over many other ligands are the relative easiness of preparation, high variability of electronic and steric parameters and the strong σ-donor ability of these ligands to the metal.[7,8] Moreover, Ni/NHC complexes are considered as a convenient alternative to highly expensive palladium, rhodium or other noble metal complexes.[9,10] In some cases, Ni/NHC complexes provide unique catalytic activity inaccessible for noble metal catalysts.[9–12]

A group of Ni/NHC complexes with the general formula (NHC)Ni(Cp)X also defined as half-sandwich Ni/NHC complexes has found a widespread use in catalysis.[13–15] To date, the most widely applied strategies to access (NHC)Ni(Cp)X complexes are based on traditional solution chemistry in anaerobic atmosphere by reactions of azolium salts NHC·HX (NHC proligands) with nickelocene.[15] The reaction occurs without a base because nickelocene (the metal source) already contains an embedded base. However, the synthesis of these complexes is complicated by the need to apply toxic solvents, heating of the reaction mixture and the use of inert atmosphere. Therefore, development of the operationally simple, without using inert gas atmosphere and minimal generation of waste synthetic methods of (NHC)Ni(Cp)X complexes preparation is highly desirable.

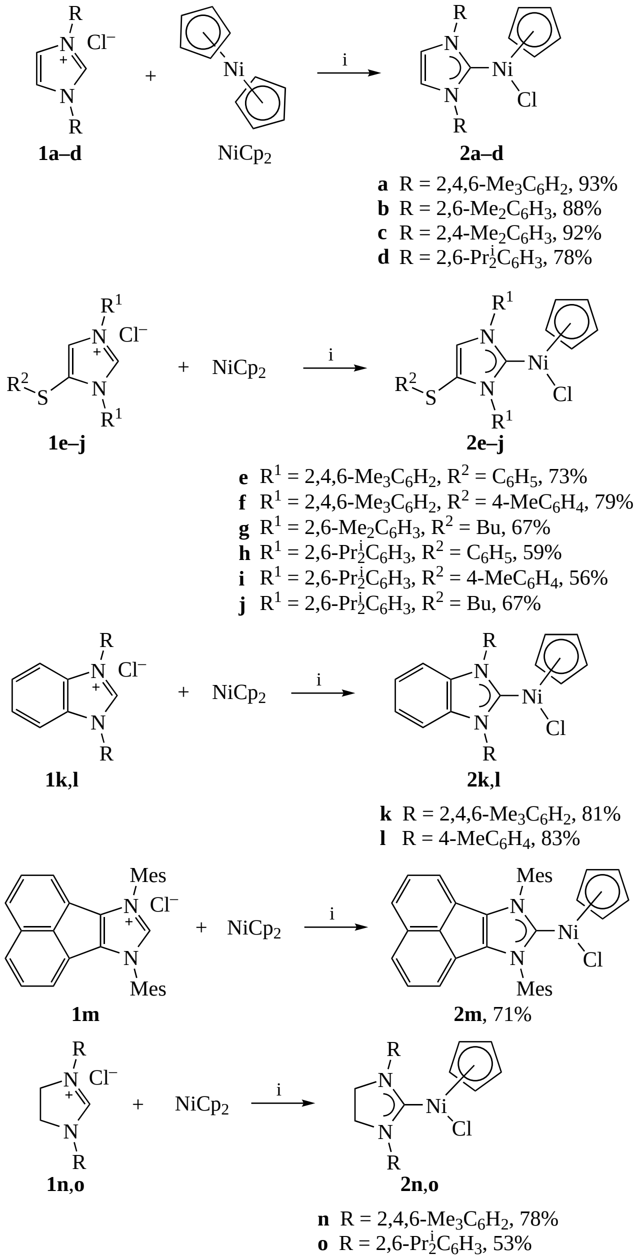
In the past years, the employment of mechanical energy to initiate chemical transformations has become an alternative synthetic method to traditional solution-based chemistry for the synthesis of numerous organometallic complexes.[16,17] Furthermore, mechanochemical methods for the synthesis of organometallic complexes are easier to operate by avoiding dry and degassed solvents, sensitive reaction conditions and inert atmosphere protection. Recently, mechanochemistry has been demonstrated as an effective tool for general, rapid and solvent-free methods for synthesis of the Ag,[18–23] Au,[18,24] Cu,[25–28] Ru,[29,30] Rh,[31] Pd[18,32,33] and Pt[34] complexes with NHC ligands. Nevertheless, to the best of our knowledge, mechanochemical syntheses of Ni/NHC complexes remain unexplored.

In the present work, we report a general method for the synthesis of (NHC)Ni(Cp)X complexes from azolium salts (the NHC-precursors) and nickelocene under mechanical activation by ball-milling in air atmosphere. Initially, we studied the model reaction between the widely used NHC precursor IMes·HCl **1a** and $NiCp_2$. We found that under ball-milling with a zirconium oxide balls and a milling jar of the same material without any additives at the maximum available operational speed (800 rpm), only a low amount of the desired product (IMes)Ni(Cp)Cl **2a** was detected after 60 min of milling (Table 1, entry 1) while the synthesis was complicated by the clumping of the reaction mixture. Therefore, in order to improve the yield of **2a**, we decided to add into the mixture small amount of solvent as a liquid assisted-grinding (LAG) additive. In the LAG mode synthesis, ratio of μl of liquid to mg of solid (η) usually falls in the range $0 < \eta < 2$.[35] After screening the common solvents such as THF, dioxane, toluene and acetonitrile in the reaction, we found that the use of 0.2 μl mg^{-1} ($\eta = 0.2$) of dioxane (entry 2) significantly improved the **2a** yield, THF (entry 3) or toluene (entry 4) insufficiently influenced the reaction, while acetonitrile (entry 5) caused complete failure of the synthesis. Moreover, a larger excess of dioxane ($\eta = 2$, see entry 2) led to decrease in the **2a** yield. Although the use of assisting liquids really improved the formation of complex **2a** in some cases, its yield never exceeded 31% (see entries 2–4). Therefore, we turned our attention to solid additives. The use of such additive as Cs_2CO_3, Na_2CO_3, K_2CO_3, $NaHCO_3$, SiO_2 or Al_2O_3 (entries 6–11) greatly improved the homogeneity of the reaction mixture and enhanced the yield of **2a**, with the K_2CO_3 additive having been of choice (entry 11). The higher yield of **2a** was observed after raising the amount of the K_2CO_3 to 2 equiv. towards the azolium salt (see

Table 1 Optimization of the reaction conditions for the synthesis of complex **2a**.[a]

Entry	Rotation speed (rpm)	LAG additive (η/μl mg^{-1})[b]	Solid additive (equiv.)[c]	Yield of **2a** (%)[d]
1	800	–	–	19
2	800	Dioxane (0.2/2)	–	31/22
3	800	THF (0.2)	–	24
4	800	Toluene (0.2)	–	26
5	800	MeCN (0.2)	–	trace
6	800	–	Cs_2CO_3 (1)	42
7	800	–	Na_2CO_3 (1)	34
8	800	–	$NaHCO_3$ (1)	28
9	800	–	SiO_2 (1)	23
10	800	–	Al_2O_3 (1)	26
11	800	–	K_2CO_3 (1/0.5)	63/34
12	800	–	K_2CO_3 (2)	91 (94[e])
13	800	–	K_2CO_3 (3)	89
14	800	–	$K_2CO_3 \cdot 1.5\,H_2O$ (1)	14
15	650	–	K_2CO_3 (2)	93 (67[f])
16	450	–	K_2CO_3 (2)	32

[a] *Reagents and conditions*: **1a** (0.5 mmol), nickelocene (0.55 mmol), additive, ball milling in air atmosphere, 60 min. [b] Microliters of liquid per mg of solid. [c] Moles of solid salt per 1 mol of azolium salt (equiv.). [d] Isolated yield. [e] In argon atmosphere. [f] 30 min milling.



Scheme 1 *Reagents and conditions*: i, **1a**–**o** (0.5 mmol), nickelocene (0.55 mmol), K_2CO_3 (1 mmol), ball milling in air atmosphere, 650 rpm, 60 min (for **2a**–**c**,**e**–**n**) or 90 min (for **2d**,**o**).

entries 11–13). The reaction proceeded well in open air without any special precautions, implementation of the reaction under argon atmosphere resulted in only insignificant increase of the yield of **2a** (see entry 12). Presumably, the positive effect of the K_2CO_3 additive was not only to reduce the clumping of the reaction mixture, but it also acted as a desiccant agent. In a control experiment on the influence of water on the synthesis, it was shown that the use of sesquihydrated potassium carbonate ($K_2CO_3 \cdot 1.5\,H_2O$) remarkably suppressed the formation of **2a** (entry 14). The optimum milling speed was found to be 650 rpm (entry 15), lower speed led to a significant reduction in the yield of **2a** (compare entries 15 and 16). A decrease in the synthesis time to 30 min resulted in a lower yield (see footnote to entry 15). Therefore, the conditions of entry 15 were accepted as optimal.

To further highlight the versatility of the methodology, the nature of the NHC proligands was varied (Scheme 1). We found that the developed protocol enabled the efficient preparation of a series of (NHC)Ni(Cp)X complexes **2a**–**o** applying various *N*,*N'*-diaryl azolium salts, such as imidazolium **1a**–**d**, those bearing potentially reactive aryl(alkyl)sulfanyl RS groups in the position 4 of the imidazole ring (**1e**–**j**), benzimidazolium (**1k**,**l**), acenaphtho[1,2-*d*]imidazolium (**1m**) and imidazolinium (**1n**,**o**) chlorides. The formation of Ni/NHC complexes was significantly dependent on the size of *N*-aryl substituents in the azolium salts, apparently due to steric factors. For example, a range of Ni/NHC complexes **2a**–**c** containing less bulky NHC ligands with xylyl or mesityl substituents on the N atoms of the imidazole core could be obtained with good yields of 88–93%, however the highest yield of complex **2d** with bulkier 2,6-diisopropylphenyl groups was only 78% and the reaction proceeded for a longer time (90 min). Complexes **2e**–**j** containing R–S groups in imidazole rings of the NHC ligand were synthesized with 56–79% yields. It is quite possible that the lower yields of complexes **2e**–**j** compared to complexes **2a**,**b**,**d** could be explained by the increased steric bulkiness of the NHC ligand due to the buttressing effect of the R–S groups on the N-aryl groups and the decreased reactivity of the NHC precursors in the nickelation reaction due to steric factors. Acenaphtho[1,2-*d*]imidazolium and imidazolinium chlorides **1m**–**o** were also tested as NHC precursors, however complexes **2m**–**o** were obtained in yields of 71, 78 and 53%, and attempts to improve these yields were unsuccessful.

All (NHC)Ni(Cp)Cl complexes **2a**–**o** were obtained as red colored air insensitive powders. Complexes **2a**,**d**,**e**,**h**,**k**,**l**,**n**,**o** were previously described in the literature,[36–40] the structures of the new complexes **2b**,**c**,**f**,**g**,**i**,**j**,**m** were confirmed by ^{1}H and ^{13}C NMR spectra and elemental analysis. The ^{1}H and ^{13}C NMR spectra of complexes **2b**,**c**,**f**,**g**,**i**,**j**,**m** are similar to those of the reported related complexes and contain characteristic singlets of one η^5-bonded Cp ring (~4.4–4.7 ppm in ^{1}H NMR, ~89.2–92.8 ppm in ^{13}C).

In order to increase the usefulness of the mechanochemical methodology, we demonstrated that the developed procedure for obtaining (NHC)Ni(Cp)Cl complexes could be scaled up, albeit with slightly lower yields, using a 45 ml zirconia reactor and loading it with 21 g of milling balls. For example, complexes **2a** were obtained with a yield of 89% by milling the nickelocene and the azolium salt **1a** in 2 mmol scale in the presence of K_2CO_3 (2 equiv.) at 650 rpm for 90 min. To our opinion, even though the overall yield of the Ni complex **2a** is not better than the best yields reported in the literature, the milling conditions are more user-friendly since no reaction solvent is used and therefore no solvent distillation is required, the only solvent being used for the recovery of the final pure compound. Moreover, inert atmosphere is not required, allowing the entire procedure to be carried out in air.

In conclusion, we have developed a new solvent-free mechanochemical one-pot procedure for the preparation of (NHC)NiCpCl complexes. The reaction is complete with good yields in the presence of solid additive K_2CO_3, without using assisted liquids. The developed process is tolerant to air oxygen as well as to functional groups in NHC ligands. Finally, the synthesis is amenable to scaling up by using a planetary ball-mill machine with larger milling reactor.

This work was supported by the Russian Science Foundation (grant no. 24-23-00424). The authors are grateful to Academician of the Russian Academy of Sciences, Professor V. P. Ananikov for a fruitful discussion of the results of this work and valuable comments. The authors also thank the Shared Research Center ‘Nanotechnologies’ of the Platov South-Russian State Polytechnic University, and the Shared Research Center of Zelinsky Institute of Organic Chemistry for analytical services.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.10.017.

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Received: 25th June 2024; Com. 24/7554