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Exploring the reactivity of nickel complexes in hydrodecyanation reactions

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ABSTRACT

In the present study, the nickel-catalyzed hydrodecyanation of organic cyanides with lithium borohydride as a cheap hydride source has been examined in detail. As precatalysts straightforward nickel complexes modified by tridentate *O,N,O′*-ligands and triphenylphosphane as co-ligand have been applied. Noteworthy, excellent yields and chemoselectivities were feasible for a variety of organic cyanides at low catalyst loadings and low temperature (70 °C) within short reaction time (3 h).

1. Introduction

Synthetic transformations supported by the aid of directing groups are well established methodologies in organic chemistry [1]. For instance organic cyano functionalities have been proven to be valuable tools, for e.g., α-acidity and *ortho*-directing effects, to access a wide range of products [2,3]. In this context, after the directing groups fulfilled their obligations different subsequent treatments have been presented, e.g., the unmodified conservation in the product, the post-functionalization or the removal. Especially, the removal is of great interest and until now various protocols have been reported for the hydrodecyanation of organic cyanides [4]. For instance excellent performances have been realized with the help of metal-based catalysts [5]. Interestingly, the application of nickel catalysts in hydrodecyanation reactions has been less investigated so far, which is in contrast to the application of cyanide functions as leaving groups for C–C and C–P cross coupling reactions [6]. Recently, the group of Maiti demonstrated the potential of the nickel-catalyzed decyanation of inert carbon–cyano bonds using *in situ* generated nickel phosphane complexes and hydrosilanes as hydride source [7,8]. To activate the cyano group and to facilitate the oxidative addition of the nickel into the C–CN bond the Lewis acid $AlMe_3$ (up to 3.0 equiv.) was added. However, high catalyst loadings (nickel source: 15–30 mol%; ligand: 30–90 mol%) and high reaction temperatures (130 °C) are required to realize reasonable amounts of product. More recently, we reported the application of well-defined nickel complexes **4** in the hydrodecyanation of organic cyanides at lower catalyst loadings (5.0 mol%) and under mild reaction conditions (70 °C) (Scheme 1b) [9]. As reductant *tert*-butylmagnesium chloride was applied. This potentially generates via transmetalation and β-hydride elimination catalytic active nickel-hydride species for the cleavage of the C–CN bond. However, long reaction times are required to achieve reasonable amounts of product, e.g., for the model substrate 4-methoxybenzonitrile 48 h are necessary to achieve 74% yield of anisole. Supposably the formation of the nickel-hydride intermediate via transmetalation and β-hydride elimination is slow, hence the overall rate is low [10]. Based on these initial achievements the development of more efficient systems is still a challenging task. To overcome the limitations in activity of our earlier protocol we wondered if it is possible to apply more reactive hydride sources, such as metal borohydrides, which have been shown to easily produce nickel hydride complexes (Scheme 1c) [11]. Advantageously, the nickel hydride should be directly accessible in one step

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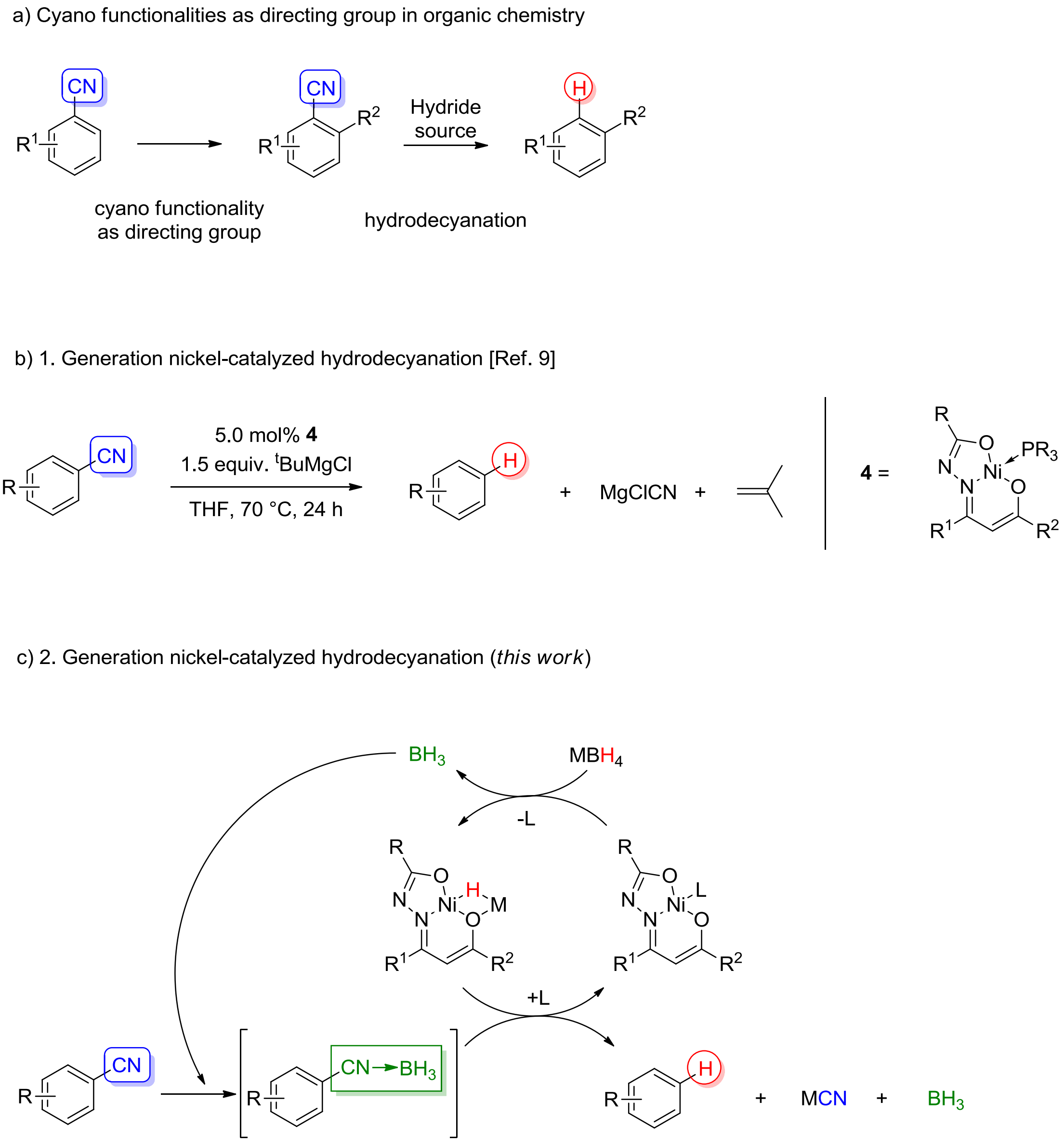


Scheme 1. Cyano functionalities as directing group in organic chemistry and nickel-catalyzed hydrodecyanation protocols.

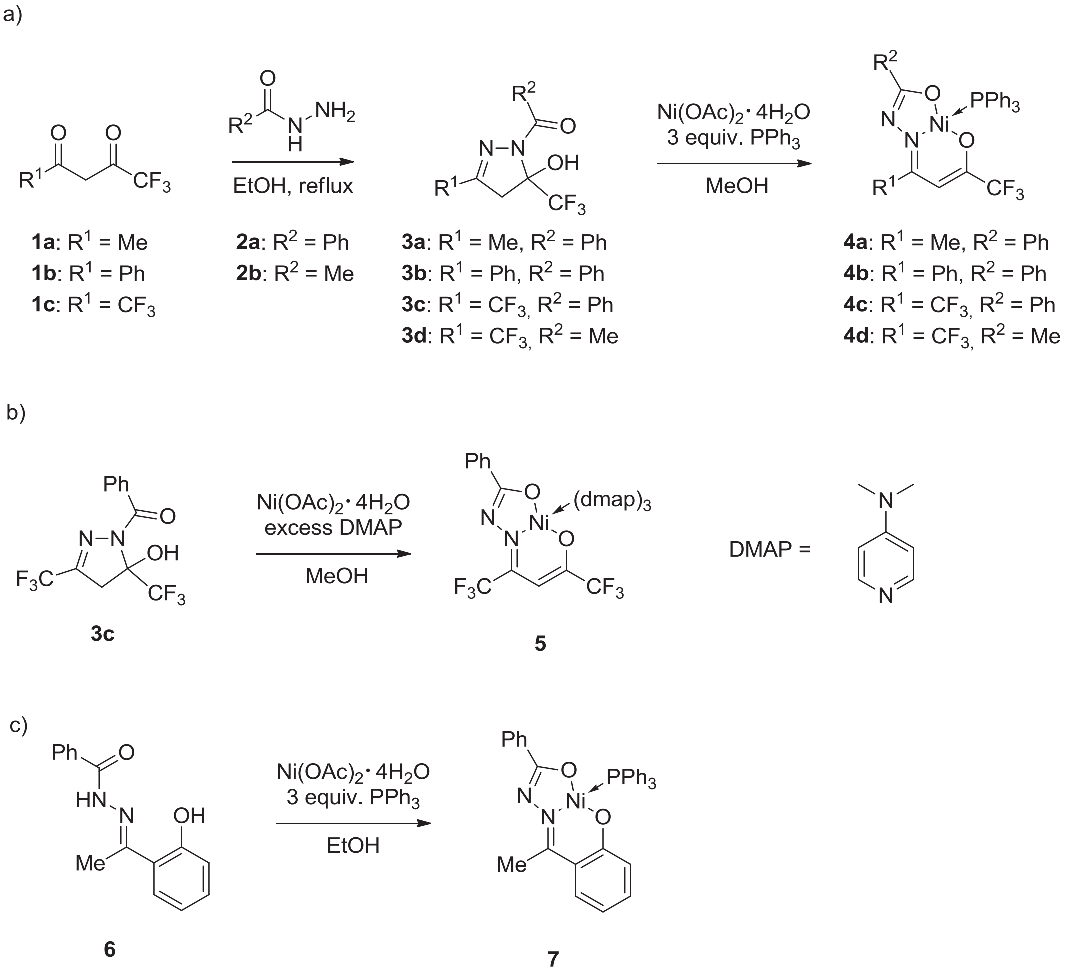
and as side product borane (BH_3) is formed, which can potentially act as a Lewis acid to activate the C–CN function and increases the overall activity of the method [6b,12]. Moreover, a cost-saving and more environmental friendly protocol should be feasible with lithium or sodium borohydrides compared to earlier approaches [13,14].

Based on that concept, we report herein our ongoing studies on the nickel-catalyzed hydrodecyanation of organic cyanides applying metal borohydrides as hydride source.

2. Results and discussion

The precatalysts **4c**, **4d**, and **5** were synthesized in accordance with our previously established protocol (Scheme 2a and b) [9,10,15]. Moreover, complex **7** was obtained by the method reported by Dharmaraj and co-workers with slight modifications (Scheme 2c) [16]. The new precatalysts **4a** and **4b** were synthesized following the reported method (Scheme 2a) [9,10,15]. A methanol solution of ligands **3**, which were accessible by the reaction of the corresponding diketone with benzohydrazide, and an excess of triphenylphosphane (3.0 equiv.) was added to a solution of $Ni(OAc)_2 \cdot 4H_2O$ in methanol at room temperature. After stirring overnight, all volatiles were removed in vacuum to obtain brown powders, which were extracted with ethanol and purified by crystallization to obtain brown crystals in fair to good yields (**4a**: 59%, **4b**: 21%).

Crystals suitable for X-ray measurements were grown from *n*-hexane by slow evaporation of the solvent at room temperature. The solid-state structures of complexes **4a** and **4b** have been characterized by single-crystal X-ray diffraction analysis. Thermal ellipsoid plots, selected bond lengths and angles are shown in Figs. 1 and 2. In agreement with the work of the Joshi group, and previous work by our group, square planar arrangements were observed for the nickel–PPh_3 complexes **4a** and **4b** with similar bond lengths and angles [9,10,15,17,18]. The tridentate ligand is coordinated in a *O,N,O′*-mode creating a five-membered and a six-membered ring system. The triphenylphosphane ligand is *cis*-positioned to the oxygen donors, while the nitrogen of the



Scheme 2. Synthesis of the hydrodecyanation precatalysts.

5-hydroxypyrazoline ligand connected to the nickel is *trans*-positioned. Moreover, the molecular structure of **7** is in agreement with the structure reported by Dharmaraj and co-workers and the bond lengths and bond angles are comparable to **4a** and **4b** [16].

After the synthesis and characterization of the nickel complexes we directed our attention to the formation of nickel-hydride species based on those complexes; **4a** was chosen as model complex. In our earlier study we have assumed that for the hydrodecyanation the hydride source is *tert*-butylmagnesium chloride and the process proceeds via nickel-alkyl intermediates (**4c**–**2a**, **4c**–**2b**) that undergo subsequent β-hydride elimination leading to nickel-hydride complexes (**4c**–**3a**, **4c**–**3b**) as crucial intermediates (Scheme 3). However, it was not possible to detect nickel-hydride intermediates for instance by ^{1}H NMR. One reason can be the slow formation of the nickel hydride by β-hydride elimination. To force this formation a higher temperature was required, at which the nickel hydride decomposes rapidly if no substrate is available. To overcome the limitations of the β-hydride elimination, lithium borohydride was applied as hydride source, which should directly form the corresponding nickel hydride complex [11]. Indeed, the reaction of the nickel complex **4a** with equimolar amounts of $LiBH_4$ in THF-d_8 for 2 min at 70 °C showed a color change from orange to green. The sample was immediately frozen with liquid nitrogen and investigated with VT (Variable Temperature) NMR techniques. Importantly, heating for a longer time resulted in the formation of a black precipitate, which was also true for standing the solution for 1 h at room temperature. First, $^{31}P\{^1H\}$ NMR measurements revealed the formation of free PPh_3. In the ^{1}H NMR ($T = -50$ °C) two broad signals were observed with chemical shifts of −31.02 ppm and −25.44 ppm in a ratio of 1:4.8, which can probably be attributed to the potential nickel hydride species (**4a**–**2a**, **4a**–**2b**), while the signals for $LiBH_4$ [$\delta = -0.53$ ppm (m)], BH_3 [$BH_3 \cdot THF$ $\delta = 2.74$ ppm (br)] [19] or LiH [20] are in a different range. Performing the measurement at 25 °C one broad signal was observed at $\delta = -19.39$ ppm besides a minor signal at $\delta = -21.23$ ppm. Importantly, the signals can also be attributed to nickel borohydride complexes (η^1-coordination: **4a**–**3a**, **4a**–**3b**, η^2-coordination: **4a**–**3c**, **4a**–**3d**) and the presence of those complexes cannot be ruled out [11b,21]. Due to the broadness of the signals no coupling patterns are visible. The broadness of the signals can arise from exchange reactions or by paramagnetism of the nickel center (coordination of solvent molecules can form octahedral complexes). Moreover, in the ^{7}Li NMR two signals were observed with a chemical shift of −106.9 ppm and −79.6 ppm. Along with the two signals, $LiBH_4$ was detected at $\delta = -0.7$ ppm.

To prove the reactivity of the formed species in hydrodecyanation reactions 4-fluorobenzonitrile (5 equiv.) was added to the mixture of complex **4a** and $LiBH_4$ (10 equiv.) after 2 min at 70 °C (Scheme 4). The mixture was reacted at 70 °C for 10 min and subsequent NMR measurements were carried out at room temperature. The formation of the hydrodecyanation product fluorobenzene (**8a**) was detected by ^{19}F NMR showing the appearance of a new signal at $\delta = -116.2$(m) ppm, while the peak corresponding to **8** is decreasing ($\delta = -106.7$(m) ppm). Noteworthy, a

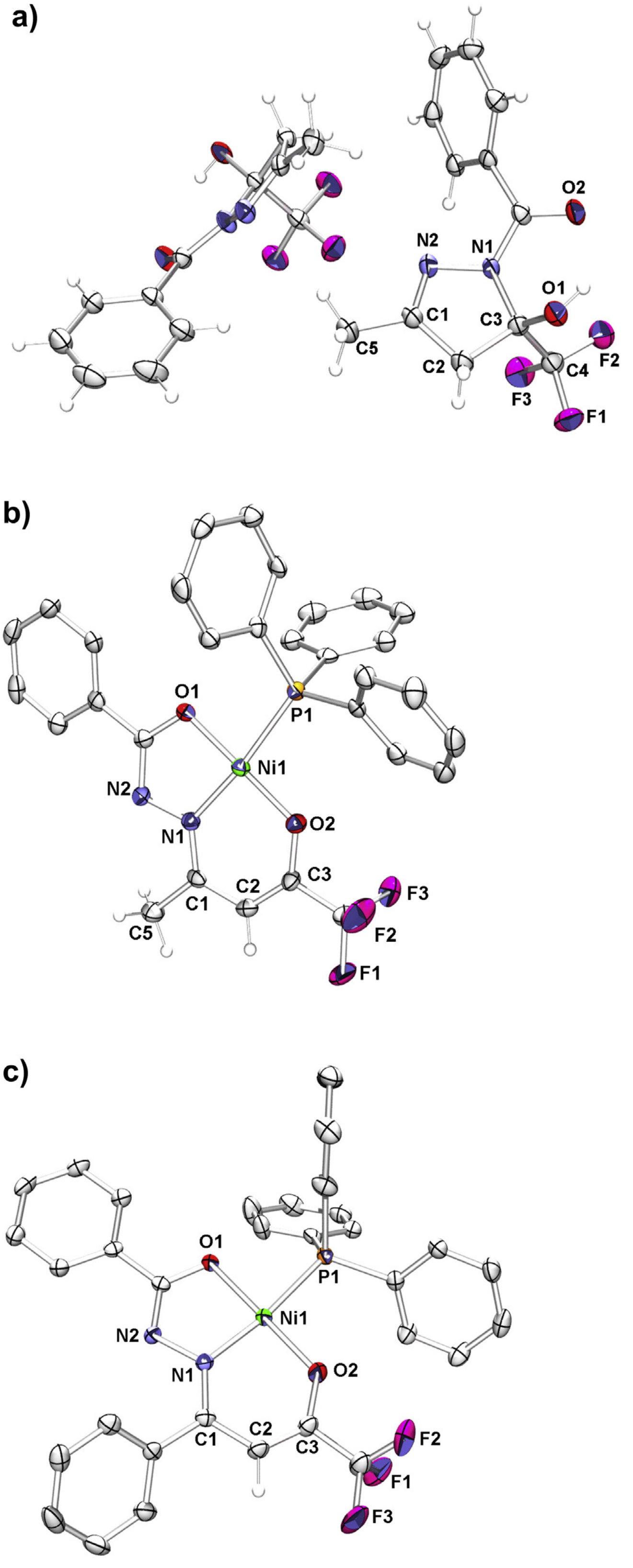


Fig. 1. Molecular structures of **3a** (a), **4a** (b), and **4b** (c). Thermal ellipsoids are drawn at the 50% probability level. Most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] of **3a**: N(1)–N(2): 1.422(2), N(1)–C(3): 1.486(2), N(2)–C(1): 1.282(2), C(1)–C(2): 1.492(3), C(2)–C(3): 1.533(3), C(3)–C(4): 1.532(3), C(1)–C(5): 1.494(3); **4a** (for clarity only one molecule of the unit cell is presented): Ni(1)–O(1): 1.820(2), Ni(1)–O(2): 1.816(2), Ni(1)–N(1): 1.855(3), Ni(1)–P(1): 2.2263(11), N(1)–N(2): 1.408(3), O(2)–C(3): 1.226(2), O(1)–Ni–O(2): 179.31(11), N(1)–Ni–P(1): 172.23(9). **4b** (for clarity only one molecule of the unit cell is presented): Ni(1)–O(2): 1.8235(16), Ni(1)–O(1): 1.8389(15), Ni(1)–N(1): 1.8729(16), Ni(1)–P(1): 2.2422(6), N(1)–N(2): 1.393(2), O(2)–C(3): 1.307(3), O(1)–Ni(1)–O(2): 179.14(7), N(1)–Ni(1)–P(1): 172.68(6).

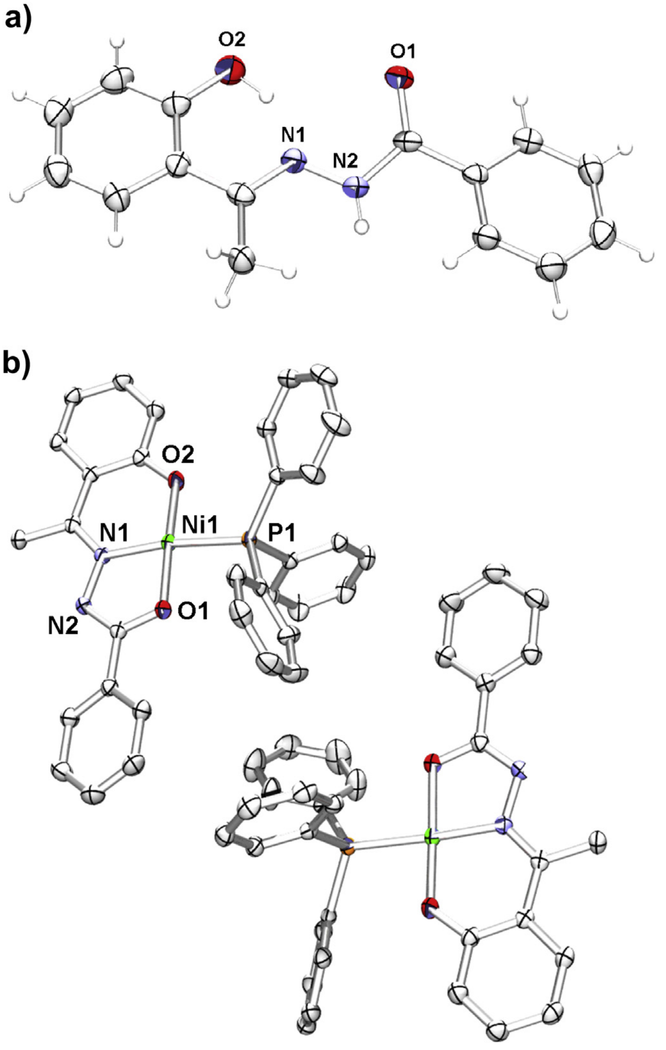
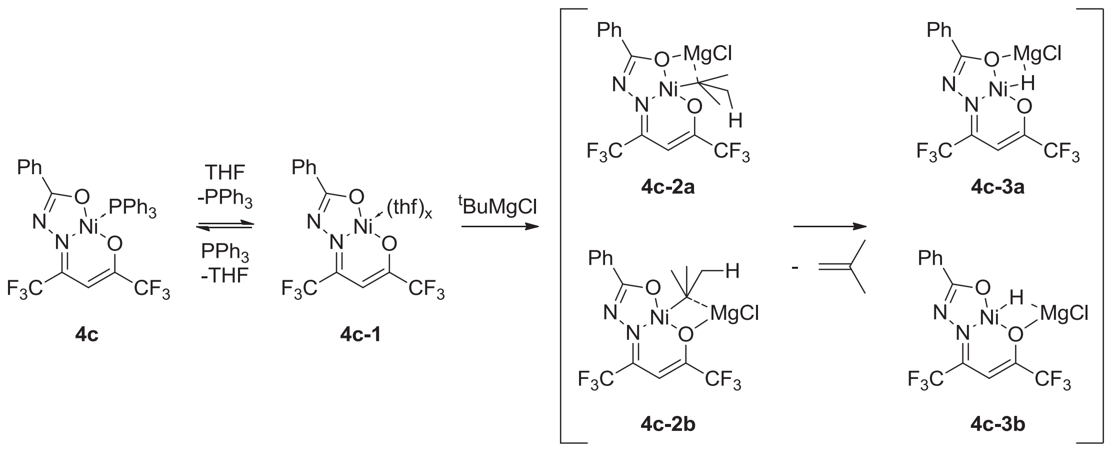


Fig. 2. Molecular structures of **6** (a) and **7** (b). Thermal ellipsoids are drawn at the 50% probability level. **7**: Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] of **6**: N(1)–N(2): 1.379(3), **7** [16]: Ni(1)–O(1): 1.8355(11), Ni(1)–O(2): 1.8122(11), Ni(1)–N(1): 1.8668(13), Ni(1)–P(1): 2.2385(5), O(1)–Ni(1)–O(2): 175.50(6), N(1)–Ni(1)–P(1): 171.92(4).

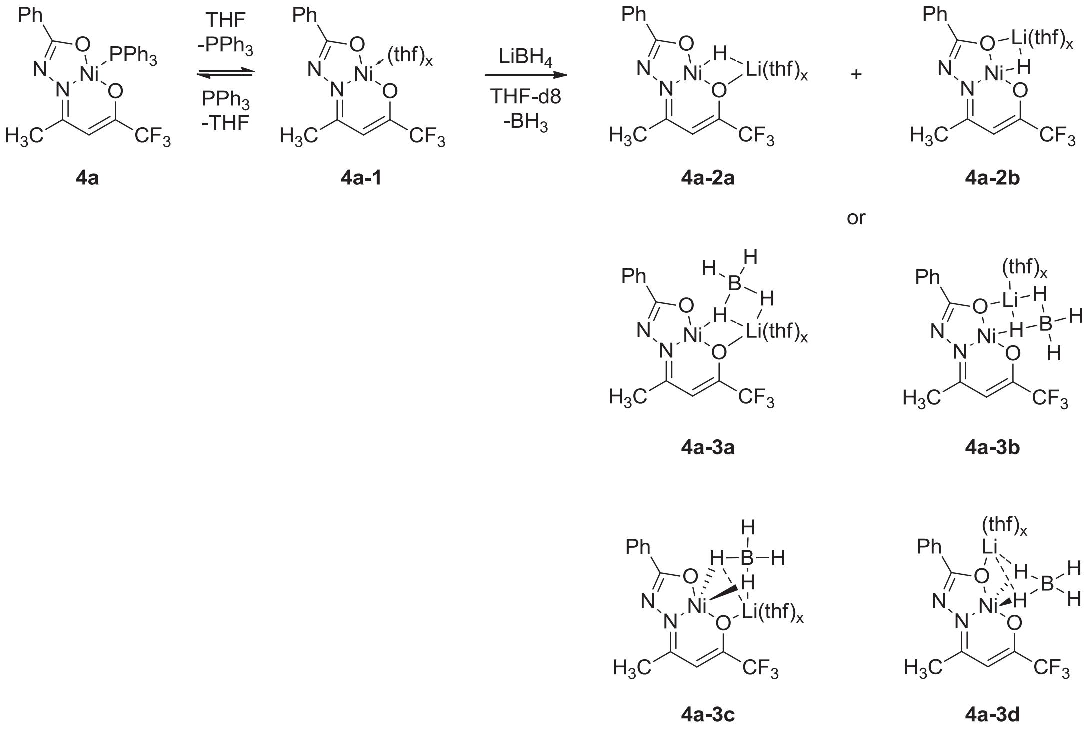
yield of 66% was observed after 10 min proving the catalytic activity of the complex. Moreover, in the ^{1}H NMR one broad signal was observed at $\delta = -19.39$ ppm and a minor signal at $\delta = -21.23$ ppm, which can be attributed to nickel-hydride or nickel-borohydride species (Scheme 3, **4a**–**2** and **4a**–**3**).

Moreover, IR measurements were carried out to study a potential activation of the cyano group. In more detail, a solution of 4-methoxybenzonitrile (**9**) in THF was mixed with $LiBH_4$, complex **4a**, or $BH_3 \cdot THF$. Only in case of $BH_3 \cdot THF$ a new band was detected at 2236 cm^{-1}, which indicates the activation of the cyano group by the Lewis acid $BH_3 \cdot THF$, while for all other reagents the band of the cyano group was unchanged (2225 cm^{-1}). The weakening of the C–CN bond by BH_3 is further indicated by comparing the calculated bond-dissociation energies (*BDE*s) of benzonitrile (*BDE* = 555.6 kJ mol^{-1}) and of the benzonitrile-BH_3 adduct complex (*BDE* = 447.0 kJ mol^{-1})

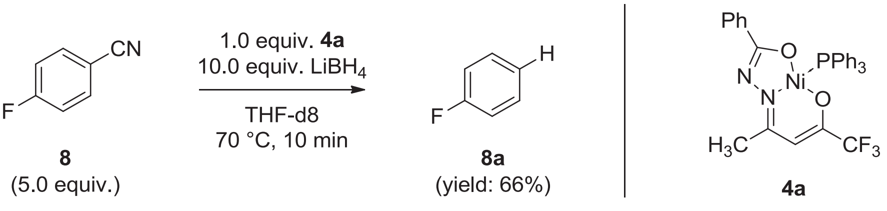
a) 1. Generation hydrodecyanation



b) 2. Generation hydrodecyanation



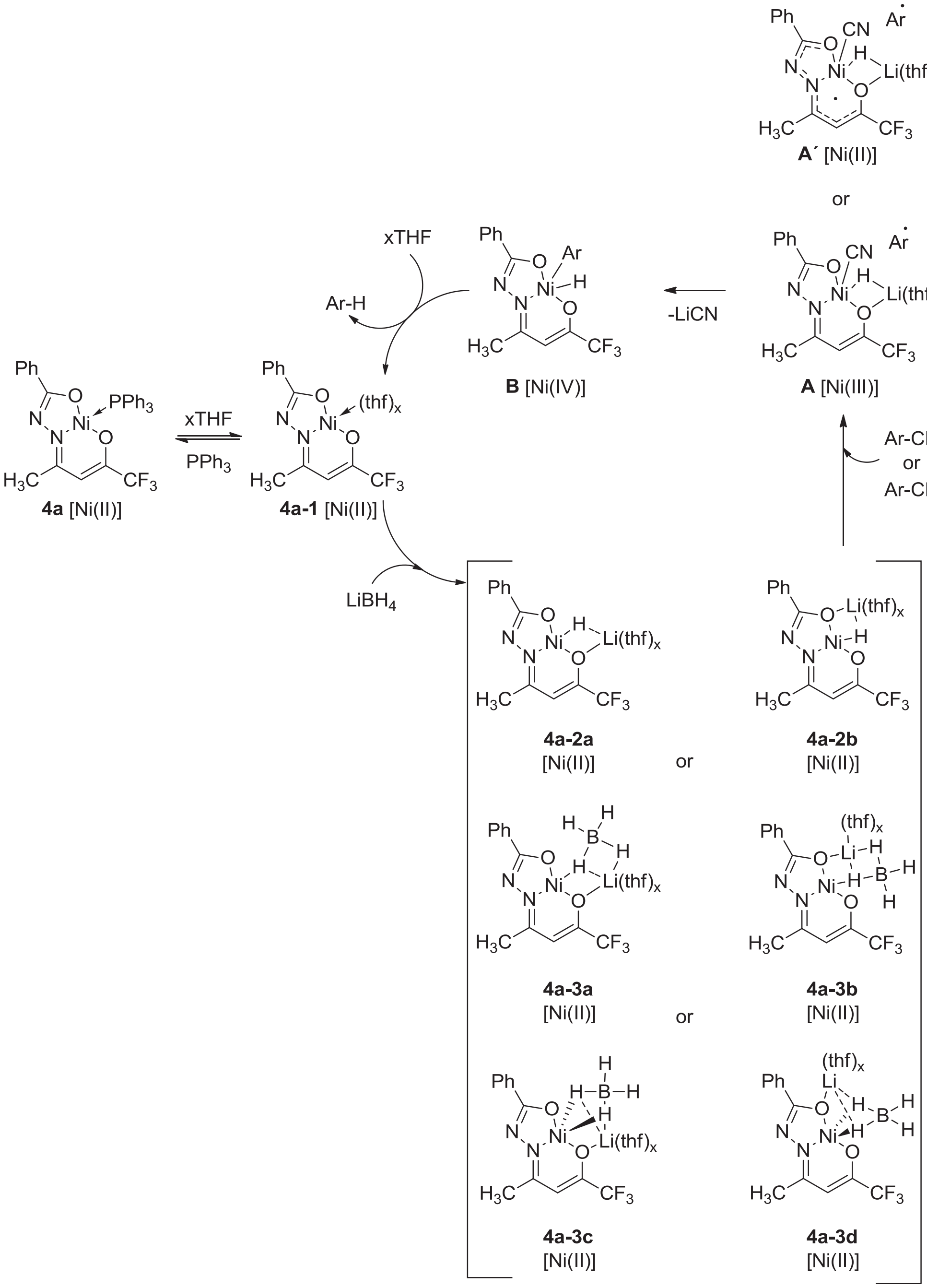
Scheme 3. Formation of potential nickel-hydride/borohydride species.



Scheme 4. Hydrodecyanation of 4-fluorobenzonitrile (**8**).

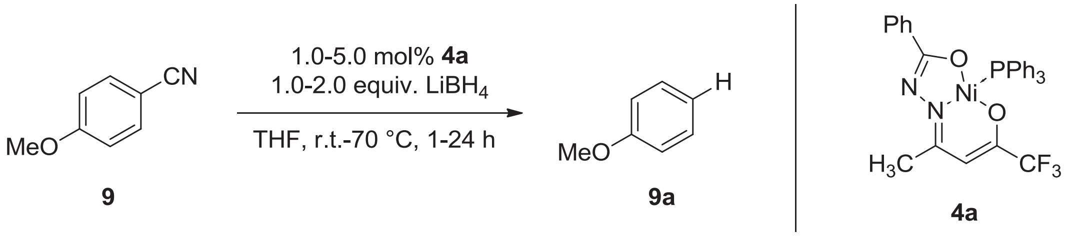
[22]. Based on the preliminary investigations we propose a reaction mechanism as presented in Scheme 5. First the triphenylphosphane ligand dissociates from complexes **4a** to create open coordination sites, which are temporarily occupied by solvent molecules. The complex **4a**–**1** reacts with the lithium borohydride to form the nickel hydride (**4a**–**2a**, **4a**–**2b**) or nickel borohydride intermediates (**4a**–**3a**, **4a**–**3b**, **4a**–**3c**, **4a**–**3d**). The organic cyanide or the Lewis acid activated cyanide approaches the coordination sphere of the nickel and mediates a single electron transfer (SET) to oxidize the complex and produce a radical [23]. The one-electron oxidized complex can on the one hand oxidized at the metal center or on the other hand the electron can be stored in the ligand (non-innocent ligand). Subsequently, lithium cyanide is eliminated and the radical recombines with the nickel species to form the species B [24]. Finally, an elimination of Ar–H occurs to regenerate complex **4a**–**1**.

After isolation, characterization and proving the reactivity of complex **4a** in hydrodecyanation the reaction conditions were investigated in more detail (Table 1). As model reaction the hydrodecyanation of 4-methoxybenzonitrile (**9**) with 2 equiv. $LiBH_4$ was studied. First, the hydrodecyanation was performed in the presence of 5.0 mol% **4a** resulting in an excellent yield of anisole (**9a**) of >99% after 24 h at 70 °C (Table 1, entry 2). Noteworthy, the addition of the nickel complex was necessary to perform the reaction, while in the absence no product formation was monitored (Table 1, entry 1). Importantly, an excellent selectivity for the cleavage of the C–CN bond was observed, while the reduction of



Scheme 5. Proposed catalytic cycle for the nickel-catalyzed hydrodecyanation.

Table 1
Nickel-catalyzed hydrodecyanation of 4-methoxybenzonitrile (**9**).



Entry[a]	Catalyst loading [mol%]	T [°C]	t [h]	Yield [%][b]
1	–	70	24	<1
2	5.0	70	24	>99
3	2.5	70	14	>99
4	2.5	70	3	>99
5	1.0	70	14	>99
6	2.5	70	1	24
7	2.5	40	3	<1
8	2.5	RT	14	<1
9[c]	2.5	70	3	43
10[d]	2.5	70	3	<1
11[e]	2.5	70	24	<1
12[d,f]	2.5	70	1	<1
13[d,g]	2.5	70	1	<1
14[d,h]	2.5	70	1	<1
15[d,i]	2.5	70	1	<1

[a] Reaction conditions: **9** (1.0 mmol), precatalyst **4a** (1.0–5.0 mol%), $LiBH_4$ (1.0–2.0 equiv.), THF (5.0 mL), r.t.–70 °C, 1–24 h.

[b] Determined by GC–MS applying *n*-dodecane as internal standard.

[c] 1.0 equiv. $LiBH_4$.

[d] 2.0 equiv. $NaBH_4$.

[e] 2.0 equiv. $LiBHEt_3$.

[f] 1,4-Dioxane as solvent and complex **4c** as precatalyst.

[g] 1,2-Dimethoxyethane as solvent and complex **4c** as precatalyst.

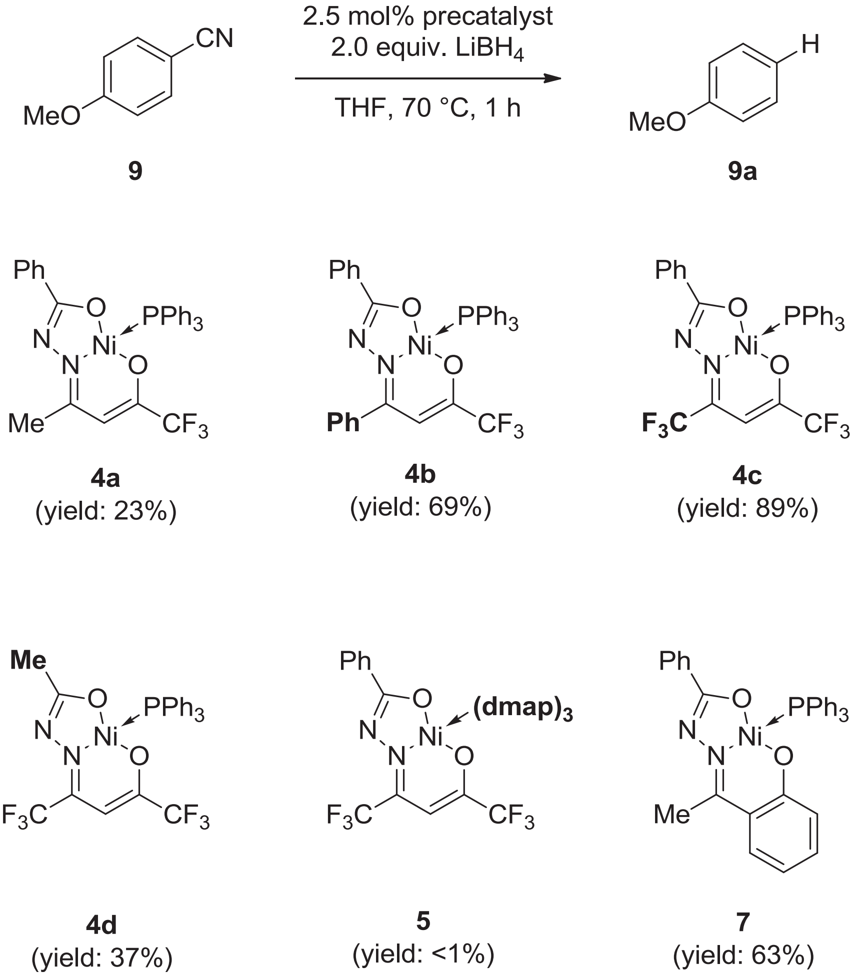
[h] Diethylene glycol dimethyl ether as solvent and complex **4c** as precatalyst.

[i] 2.0 equiv. of LiOOCH.

the C–N triple bond by $LiBH_4$ or BH_3 did not occur [25]. Decreasing the catalyst loading to 2.5 mol% or 1.0 mol%, respectively, resulted in an excellent yield after 14 h (Table 1, entries 3–5). With 2.5 mol% of **4a** full conversion was realized after 3 h, while after 1 h 24% yield of anisole (**9a**) was detected (Table 1, entries 4 and 6, respectively). Decreasing the reaction temperature to 40 °C or room temperature no product formation was noticed (Table 1, entries 7 and 8, respectively). Reducing the amount of $LiBH_4$ to 1 equiv. showed a diminished yield of 43% after 3 h (Table 1, entry 9). A change of the hydride source $LiBH_4$ to $NaBH_4$ resulted in no product formation, probably due to poor solubility in THF and lower activity of the $NaBH_4$ (Table 1, entry 10).

Next, the structure–activity relationship was investigated, applying complexes **4**, **5** and **7** as precatalysts in the hydrodecyanation of 4-methoxybenzonitrile (**9**) (Scheme 6). The reaction conditions are in accordance to Table 1 entry 6. Interestingly, substitution of the methyl group by a phenyl group (complex **4b**) resulted in an increase of the yield of **9a** to 69%. Probably the phenyl substituent allows for a better stabilization of the intermediates in the catalytic cycle by delocalization. On the other hand, substitution of the methyl group by an electron-withdrawing CF_3-group (complex **4c**) showed an excellent performance with a yield of 89% after one hour. Significantly, the obtained catalyst activity for the hydrodecyanation applying $LiBH_4$ as hydride source is superior in comparison to earlier reports, e.g., the combination of 5.0 mol% of complex **4c** and *tert*-butylmagnesium chloride as hydride source requires 48 h to reach 74% of product **9a** [9]. Moreover, the substitution of the phenyl group in **4c** by a methyl (complex **4d**) resulted in a decrease of activity, which demonstrated once more the need for aromatic substituents to realize high activities. In addition, changing the square planar geometry to an octahedral geometry (complex **5**) no product was observed. Probably, the strong coordination of the three dmap ligands and the shielding of the metal center allow not for an easy creation of free coordination sites for the substrates. Moreover, the enolate function of the complex **4a** was changed to a phenolate function (complex **7**) showing an improvement of the catalyst activity. Probably the phenyl substituent allows for a better stabilization of the intermediates in the catalytic cycle by delocalization as discussed for complex **4c**.

After investigation of the reaction conditions and the precatalyst-screening, precatalyst **4c** was applied in the hydrodecyanation of various aryl and alkyl cyanides with $LiBH_4$ as hydride source (Table 2). Excellent yields (>99%) were observed for methoxy- and methyl substituted aryl cyanides (Table 2, entries 1–5). For other functional groups such as amine, ester or thioether in *para*-position lower reactivity was observed or an attack of the functional group (Table 2, entries 6–9). In contrast, 4-fluorobenzonitrile was selectively converted to 4-fluorobenzene in excellent yield and selectivity, while for 4-bromobenzonitrile the hydrodehalogenation and hydrodecyanation were monitored (Table 2, entry 11). Moreover, 1,4-dicyanobenzene was converted with 1.1 equiv. of $LiBH_4$ in excellent selectivity to benzonitrile (Table 2, entry 13). In contrast to our first generation hydrodecyanation system most aromatic cyanides were converted in excellent yields and selectivities in short reaction times and low catalyst loadings. In addition, heteroaromatic substrates were tested resulting in excellent yield of thiophene, while 3-cyanopyridine was not converted, probably due to the coordination abilities of the pyridine (Table 2, entries 14 and 15). In case of cinnamonitrile (**24**) the reduction of the C–C double bond was



Scheme 6. Investigation of the influence of the precatalyst structure on the hydrodecyanation of **9**.

observed as major reaction pathway (Table 2, entry 12). In addition, aliphatic cyanides such as **25** and **26** were not converted to the desired product, which is in contrast to the first generation hydrodecyanation protocol. However, the reactions could be of interest for the selective removal of aromatic cyanides in the presence of aliphatic cyanides (Table 2, entry 17–18).

In addition, the hydrodecyanation protocol was embedded in the synthesis of pentamethoxybenzene (**29**), which has been applied for instance in the total synthesis of Nobiletin a biological active compound (Scheme 7) [26]. In more detail, multi-step approaches have been established to access compound **29** [26,27]. For instance Kan and co-workers reported a 8-step synthesis starting from 1,2,3-trimethoxybenzene (**10a**). An alternative approach can be the application of the commercial available compound **10** and to make use of the *ortho*-directing effect of the nitrile functionality in palladium-catalyzed alkoxylation reactions as recently reported by Li and Sun [3d]. A subsequent hydrodecyanation reaction should provide the desired target compound **29** in an overall two-step synthesis. Hence, the bisalkoxylation of **10** was performed with 10 mol% $Pd(OAc)_2$ and $Na_2S_2O_8$ (5.0 equiv.) as oxidant in methanol. After 8 h at room temperature and 16 h at 70 °C the desired product **27** was obtained in 73% yield accompanied by the monoalkoxylated compound **28**. After isolation of the product **27** it was subjected to the hydrodecyanation protocol applying the optimized conditions. After 3 h the product 1,2,3,4,5-pentamethoxybenzene (**19**) was obtained in moderate yield of 17%. Probably due to sterical and electronic effects of the methoxy groups in *ortho*-position to the cyano group the reactivity is decreased. On the other hand, the side product **28** was also subjected to hydrodecyanation to obtain compound **30** in 30% yield. Interestingly, this compound can easily converted to **29** and in consequence to Nobiletin [26].

3. Conclusion

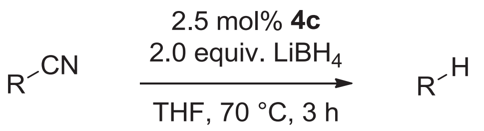
In summary, we have set up a methodology for the nickel-catalyzed hydrodecyanation of organic cyanides with $LiBH_4$ as hydride source under mild reaction conditions, with low catalyst loadings and within short times. With the well-defined nickel complex **4c** a variety of aryl cyanides were converted. Noteworthy, in comparison to our earlier work a significant improvement of the catalyst activity was observed.

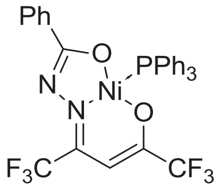
4. Experimental section

4.1. General

All compounds were used as received without further purification. THF was dried applying standard procedures. ^{1}H, ^{7}Li ^{19}F, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance II 200 spectrometer (^{1}H: 200.13 MHz; ^{13}C: 50.32 MHz; ^{19}F: 188.31 MHz, ^{31}P: 81.01 MHz, ^{7}Li: 77.78 MHz) using the proton signals of the deuterated solvents as reference. ^{1}H and ^{7}Li Variable Temperature (VT) NMR measurements were carried out on a Bruker Avance 400 spectrometer (^{1}H: 400.13 MHz; ^{7}Li: 155.54 MHz).

Table 2
Scope and limitations of the nickel-catalyzed hydrodecyanation.





4c

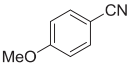
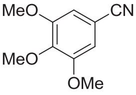
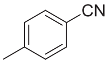
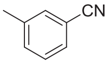
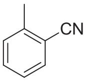
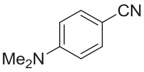
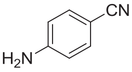
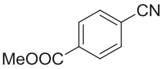
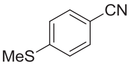
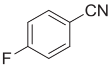
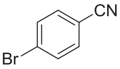
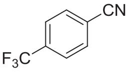
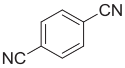
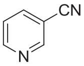
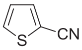
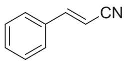
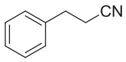
Entry[a]	Substrate	Yield [%] [Ref. [9]][b]	Selectivity [%][c]	Yield [%][d]
1	 **9**	61	>99	**9a**: >99 (89)
2	 **10**	63	>99	**10a**: >99 (94)
3	 **11**	57	>99	**11a**: >99
4	 **12**	49	>99	**11a**: >99
5	 **13**	38	>99	**11a**: >99
6	 **14**	20	>99	**14a**: 17
7	 **15**	–	–	**15a**: <1
8	 **16**	<1	–	**16a**: <1[e]
9	 **17**	74	–	**17a**: <1
10	 **8**	80	>99	**8a**: >99
11	 **19**	<1	–	**19a**: 53[f]
12	 **20**	<1	>99	**20a**: 68
13[g]	 **21**	–	97	**21a**: 97[h]
14	 **22**	–	–	**22a**: <1
15	 **23**	>99	>99	**23a**: >99

Table 2 (*continued*)

Entry[a]	Substrate	Yield [%] [Ref. [9]][b]	Selectivity [%][c]	Yield [%][d]
16	 **24**	–	–	**24a**: 87[i]
17	 **25**	–	–	**25a**: 7
18	CH$_3$(CH$_2$)$_8$CN **26**	64	–	**26a**: <1

[a] Reaction conditions: substrate (1.0 mmol), precatalyst **4c** (2.5 mol%), LiBH$_4$ (2.0 equiv.), THF (5.0 mL), 70 °C, 3 h.
[b] For comparison the yields of the 1. Generation hydrodecyanation (Ref. [9]) with 5.0 mol% **4c** and *tert*-butylmagnesium chloride after 24 h is stated.
[c] Refers to the hydrodecyanation reaction.
[d] Determined by GC–MS applying *n*-dodecane as internal standard. In brackets the isolated yield is stated.
[e] Numerous undefined products.
[f] Benzene.
[g] 1.1 equiv. LiBH$_4$.
[h] Refers to benzonitrile.
[i] Reduction of the C–C double bond.

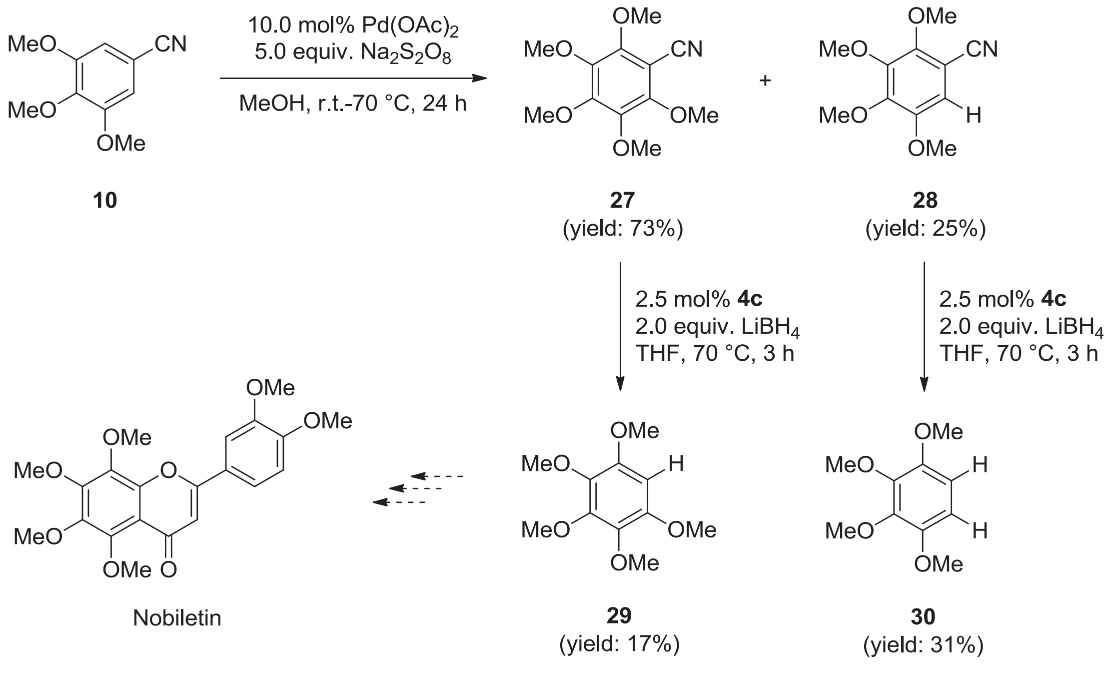
Single crystal X-Ray diffraction measurements were recorded on an Oxford Diffraction Xcalibur S Sapphire spectrometer. GC–MS measurements were carried out on a Shimadzu GC-2010 gas chromatograph (30 m Rxi-5 ms column) linked with a Shimadzu GCMA-QP 2010 Plus mass spectrometer. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR. Ligands **3c** and **3d** and complexes **4c**, **4d** and **5** were synthesized in accordance to literature protocols. [10,15].

4.1.1. *Synthesis of ligand **3a***

A mixture of benzohydrazide (65.3 mmol) and 1,1,1-trifluoropenta-2,4-dione (65.3 mmol) was dissolved in ethanol (50 mL) and stirred for 24 h at 80 °C. Subsequently the solvent was removed under reduced pressure and the colorless residue was purified by recrystallization from *n*-hexane. Crystals suitable for X-ray diffraction were obtained from a concentrated *n*-hexane solution. Yield = 40% (colorless crystals). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C) δ = 7.87–7.84 (m, 2H, Ar–H), 7.53–7.36 (m, 3H, Ar–H), 6.55 (s, br, 1H, OH), 3.32–3.04 (m, 2H, CH_2), 2.01 (s, 1H, CH$_3$) ppm. ^{13}C {^{1}H} NMR (400 MHz, CDCl$_3$, 25 °C) δ = 171.1, 154.7, 133.0, 132.1, 130.1, 127.8, 126.3, 92.4, 46.7 (CH$_2$), 15.6 (CH$_3$) ppm. ^{19}F NMR (188 MHz, CDCl$_3$, 25 °C) δ = −81.2 ppm. IR (KBr): ν = 3365 (br), 3001 (m), 1661 (s), 1635 (s), 1602 (m), 1579 (m), 1496 (m), 1452 (s), 1435 (s), 1381 (s), 1353 (s), 1334 (s), 1319 (s), 1235 (m), 1207 (s), 1180 (vs), 1156 (s), 136 (s), 1121 (s), 1100 (m), 1049 (m), 1029 (m), 997 (m), 969 (m), 892 (m), 841 (m), 825 (m), 791 (m), 755 (m), 736 (m), 717 (m), 696 (m), 671 (m), 654 (m), 620 (m), 494 (m) cm^{-1}. HRMS calcd. for C$_{12}$H$_{11}$F$_3$N$_2$O$_2$ + H: 273.08454; found 273.08499.

4.1.2. *Synthesis of complex **4a***

A mixture of **3a** (7.35 mmol), Ni(OAc)$_2$·4H$_2$O (7.35 mmol) and triphenylphosphane (14.70 mmol) was dissolved in methanol (25 mL) and stirred for 24 h at room temperature. After removal of the volatiles under reduced pressure, a brown solid was obtained. The residue was purified by recrystallization from *n*-hexane. Crystals suitable for X-ray diffraction were obtained from a



Scheme 7. Synthetic application of the hydrodecyanation protocol.

concentrated *n*-hexane solution at room temperature. Yield = 59% (brown crystals). ^{1}H NMR (200 MHz, C_6D_6, 25 °C) $\delta = 8.00–7.95$ (m, 2H, Ar–H), 7.84–7.73 (m, 6H, Ar–H), 7.13–6.99 (m, 12H, Ar–H), 5.76 (s, 1H, CH), 2.35 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) $\delta = 170.6$, 156.1, 134.3, 131.2, 130.4, 129.6, 192.2, 128.4, 128.2, 97.6, 19.0 ppm (some signals are covert by solvent signals). ^{19}F NMR (188 MHz, C_6D_6, 25 °C) $\delta = -70.9$ ppm. $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 25 °C) $\delta = 15.4$ ppm. IR (KBr): $\nu = 3436$ (br), 3058 (w), 1619 (s), 1587 (m), 1540 (s), 1520 (s), 1492 (m), 1482 (m), 1437 (s), 1371 (m), 1352 (s), 1313 (vs), 1250 (s), 1181 (s), 1143 (s), 1125 (s), 1102 (m), 1070 (m), 1028 (m), 745 (m), 694 (s), 530 (m). 509 (m), 496 (m) cm^{-1}. HRMS calcd. for $C_{30}H_{24}F_3N_2O_2NiP + H$: 591.09537; found 591.13079.

4.1.3. Synthesis of ligand **3b**

A mixture of benzohydrazide (58.8 mmol) and 4,4,4-trifluoro-1-phenylbutan-1,3-dione (58.8 mmol) was dissolved in ethanol (50 mL) and stirred for 168 h at room temperature and for 336 h at 40 °C. Subsequently the solvent was removed under reduced pressure and the colorless residue was purified by recrystallization from *n*-hexane. Yield = 29% (colorless crystals). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C) $\delta = 8.00–7.96$ (m, 2H, Ar–H), 7.64–7.33 (m, 8H, Ar–H), 6.72 (s, 1H, OH), 3.77–3.49 (m, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$, 25 °C) $\delta = 171.1$, 153.2, 133.0, 132.3, 131.1, 130.4, 129.9, 128.9, 127.9, 126.8, 126.4, 93.1, 43.1 (CH_2) ppm. ^{19}F NMR (188 MHz, $CDCl_3$, 25 °C) $\delta = -81.0$ ppm. IR (KBr): $\nu = 3372$ (br, s), 1644 (s), 1603 (m), 1577 (m), 1450 (s), 1422 (s), 1345 (s), 1309 (m), 1264 (m), 1216 (m), 1179 (s), 1126 (m), 1110 (m), 1039 (m), 1027 (m), 1005 (m), 922 (m), 902 (m), 869 (m), 759 (m), 710 (s), 688 (s), 674 (m), 598 (m), 501 (m) cm^{-1}. HRMS calculated for $C_{17}H_{13}F_3N_2O_2 + H$: 335.10019; found 335.09982.

4.1.4. Synthesis of complex **4b**

A mixture of **3b** (2.99 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (2.99 mmol) and triphenylphosphane (5.98 mmol) was dissolved in methanol (25 mL) and stirred for 24 h at room temperature. After removal of the volatiles under reduced pressure, a brown solid was obtained. The residue was purified by recrystallization from *n*-hexane. Crystals suitable for X-ray diffraction were obtained from a concentrated *n*-hexane solution at room temperature. Yield = 21% (brown crystals). ^{1}H NMR (200 MHz, C_3D_6O, 25 °C) $\delta = 7.86–7.08$ (m, 25H, Ar–H), 5.93 (s, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_3D_6O, 25 °C) $\delta = 135.7$, 134.4, 134.1, 131.0, 130.9, 129.9, 129.2, 128.8, 128.6, 128.0, 127.8, 127.7, 121.3, 115.7, 99.9, 97.4, 29.2 ppm. ^{19}F NMR (188 MHz, C_3D_6O, 25 °C) $\delta = -71.9$ ppm. $^{31}P\{^1H\}$ NMR (81 MHz, C_3D_6O, 25 °C) $\delta = 15.1$ ppm. IR (KBr): $\nu = 3435$ (br), 3056 (w), 1598 (s), 1537 (s), 1510 (m), 1485 (m), 1435 (s), 1354 (s), 1325 (s), 1308 (m), 1284 (m), 1255 (m), 1185 (s), 1167 (s), 1132 (s), 1100 (s), 1067 (m), 1027 (m), 747 (m), 693 (s), 529 (m), 509 (m) cm^{-1}. HRMS calcd. for $C_{35}H_{26}F_3N_2O_2NiP + H$: 653.11102; found 653.11163.

4.1.5. Synthesis of ligand **6** [16]

A mixture of benzhydrazide (41.7 mmol) and 2-hydroxyacetophenone (41.7 mmol) was dissolved in ethanol (50 mL) and refluxed for 24 h. A white precipitate was formed, which was filtered, washed with ethanol and dried in vacuum. Crystals suitable for X-ray diffraction were obtained from a concentrated ethanol solution at room temperature. Yield = 71% (colorless crystals). ^{1}H NMR (200 MHz, DMSO-d_6, 25 °C) $\delta = 12.38$ (s, 1H), 10.35 (s, 1H), 6.92–6.96 (m, 2H), 6.49–6.65 (m, 4H), 6.26–6.35 (m, 1H), 5.85–5.94 (m 2H), 1.48 (s, 3H, CH_3) ppm. IR (KBr): $\nu = 3204$ (m), 3043 (w), 2999 (w), 1650 (s), 1638 (s), 1611 (s), 1577 (m), 1526 (m), 1483 (m), 1450 (m), 1398 (w), 1366 (w), 1329 (w), 1304 (w), 1283 (m), 1253 (m), 1238 (s), 1158 (w), 1142 (w), 1125 (w), 1091 (w), 1075 (w), 1024 (w), 977 (w), 931 (w), 834 (m), 797 (w), 744 (s), 710 (m), 689 (m), 673 (w), 655 (w), 624 (w), 613 (w) cm^{-1}.

4.1.6. Synthesis of complex **7** [16]

A mixture of ligand **6** (2.0 mol) and $Ni(OAc)_2 \cdot 4H_2O$ (2.0 mmol) and triphenylphosphane (6.0 mmol) was dissolved in ethanol (100 mL) and stirred for 20 h at 90 °C. The mixture was filtered and the volatiles were removed under reduced pressure to obtain a red solid. The residue was purified by recrystallization from ethanol or dichloromethane. Crystals suitable for X-ray diffraction were obtained from a concentrated dichloromethane solution at room temperature. Yield = 64% (red crystals). ^{1}H NMR (200 MHz, DMSO-d_6, 25 °C) $\delta = 6.47–7.79$ (m, 24H, Ar–H), 3.28 (s, 3H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (81 MHz, DMSO-d_6, 25 °C) $\delta = 25.5$ ppm. IR (KBr): $\nu = 1575$ (m), 1529 (s), 1358 (m), 1329 (m), 1098 (m) cm^{-1}. HRMS calcd. for $C_{33}H_{27}N_2O_2NiP + H$: 573.12364; found 573.12366.

4.2. General procedure for the catalytic hydrodecyanation

A Schlenk flask was charged with an appropriate amount of complex **4c** (0.025 mmol, 2.5 mol%), $LiBH_4$ (2.0 mmol) and the corresponding organic cyanide (1.0 mmol). The flask was cycled with nitrogen and vacuum. Afterward THF (5.0 mL) was added. The flask was sealed and heated at 70 °C for 3 h. After that time, the mixture was cooled to room temperature, the THF was carefully removed in vacuum and the residue was dissolved in diethylether and filtered trough a short plug of silica. The products were confirmed by GC–MS (*n*-dodecane was added as internal standard) and NMR analysis. The analytical properties of the products are in agreement with literature data.

Fluorobenzene (**8a**): MS (EI) $m/z = 96$ (61), 70 (20), 50 (11), 44 (11), 40 (100).

Anisole (**9a**): ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 7.31–7.27$ (m, 2H), 6.96–6.86 (m, 3H), 3.79 (s, 3H) ppm. MS (EI) $m/z = 108$ (100, M^+), 93 (23), 78 (96), 65 (99), 51 (33), 40 (75).

1,2,3-Trimethoxybenzene (**10a**): ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 6.88–7.00$ (m, 1H), 6.52–6.58 (m, 2H), 3.82 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) $\delta = 153.4$, 138.1, 123.6, 105.2, 60.7, 56.0 ppm. MS (EI) $m/z = 168$ (32, M^+), 153 (33), 125 (16), 110 (21), 95 (15), 40 (100).

Toluene (**11a**): MS (EI) $m/z = 91$ (100, M^+), 89 (9), 65 (28), 63 (20), 51 (19), 40 (98).

N,N′-Dimethylaniline (**14a**): MS (EI) $m/z = 121$ (14, M^+), 40 (100).

Benzene (**19a**): MS (EI) $m/z = 78$ (64, M^+), 51 (20), 40 (20).

Trifluoromethylbenzene (**20a**): MS (EI) $m/z = 146$ (100, M^+), 127 (53), 96 (46), 77 (21).

Benzonitrile (**21a**): ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 7.35–7.66$ (m, 5H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) $\delta = 133.0$, 132.2, 129.2, 118.8, 112.2 ppm. MS (EI) $m/z = 103$ (100, M^+), 76 (39).

Thiophene (**23a**): MS (EI) $m/z = 84$ (100), 58 (76), 45 (34).

3-Phenylpropionitrile (**24a**): MS (EI) $m/z = 131$ (24, M^+), 91 (100), 65 (15).

1,2,3,4,5-Pentamethoxybenzene (**29**): MS (EI) $m/z = 228$ (100, M^+), 213 (99), 185 (24), 170 (36), 155 (22), 127 (15), 99 (13).

1,2,3,4-Tetramethoxybenzene (**30**): MS (EI) $m/z = 198$ (100, M^+), 183 (57), 168 (12), 155 (11), 140 (31), 123 (15), 95 (11), 69 (15).

Single-crystal X-ray structure determination [28]: Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data were collected using an Oxford Diffraction Xcalibur S Sapphire at 150(2) K ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) or an Agilent Technologies SuperNova (single source) at 150 K ($Cu_{K\alpha}$ radiation, $\lambda = 1.5418$ Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 software package. The positions of the hydrogen atoms were calculated and considered isotropically according to a riding model.

4.3. Computational section

Calculations were performed with the Gaussian09 program package using 6-311G** basis sets [29] and the B3PW91 level of theory [30]. Frequency calculations were performed to verify stationary points. All energies (given in kJ mol^{-1}) were corrected for (unscaled) zeropoint vibrational energy contributions. The quality of the computational protocol was proven by comparing the calculated $BDE(C_6H_5CN) = 555.6$ kJ mol^{-1} with the experimental value (555.6 kJ mol^{-1}) [31].

Acknowledgments

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Appendix A. Supplementary material

CCDC 941131, 941132, 941133, 942994 and 942995 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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