

Preparation of Nickel-on-Charcoal (Ni/C): An Improved Protocol

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Abstract: A modified preparation of the inexpensive, heterogeneous precatalyst Ni(II)/C, has been developed which (1) reduces the number of solvent distillations; (2) generates no organic waste; (3) leads to complete impregnation of the Ni(II) salts invested; and (4) extends the number of sources of

charcoal which can be used to make the catalyst. Several carbon-carbon, as well as carbon-nitrogen and carbon-hydrogen bond-forming reactions have been run which compare Ni/C prepared via this new protocol with those formed using the original protocol. The results from each are virtually identical.

The evolution of the inexpensive, heterogeneous catalyst 'nickel-on-charcoal' (Ni/C) has been discussed in the review article in this issue of the journal.^[1] Although this species originates from the operationally simple impregnation of a nickel(II) salt [in this case, Ni(NO₃)₂] onto activated carbon of a preferred 100 mesh, its processing (e.g., washing, drying, etc.) and conversion to the reduced, active Ni(0) state raises several questions of a practical nature. Issues such as charcoal type, assessment of catalyst loading, and role of organic solvent washings, have now been examined and have led to an improved and simplified preparation of Ni(II)/C. In this report, we describe this updated protocol and document the synthetic utility of the derived Ni(0)/C.

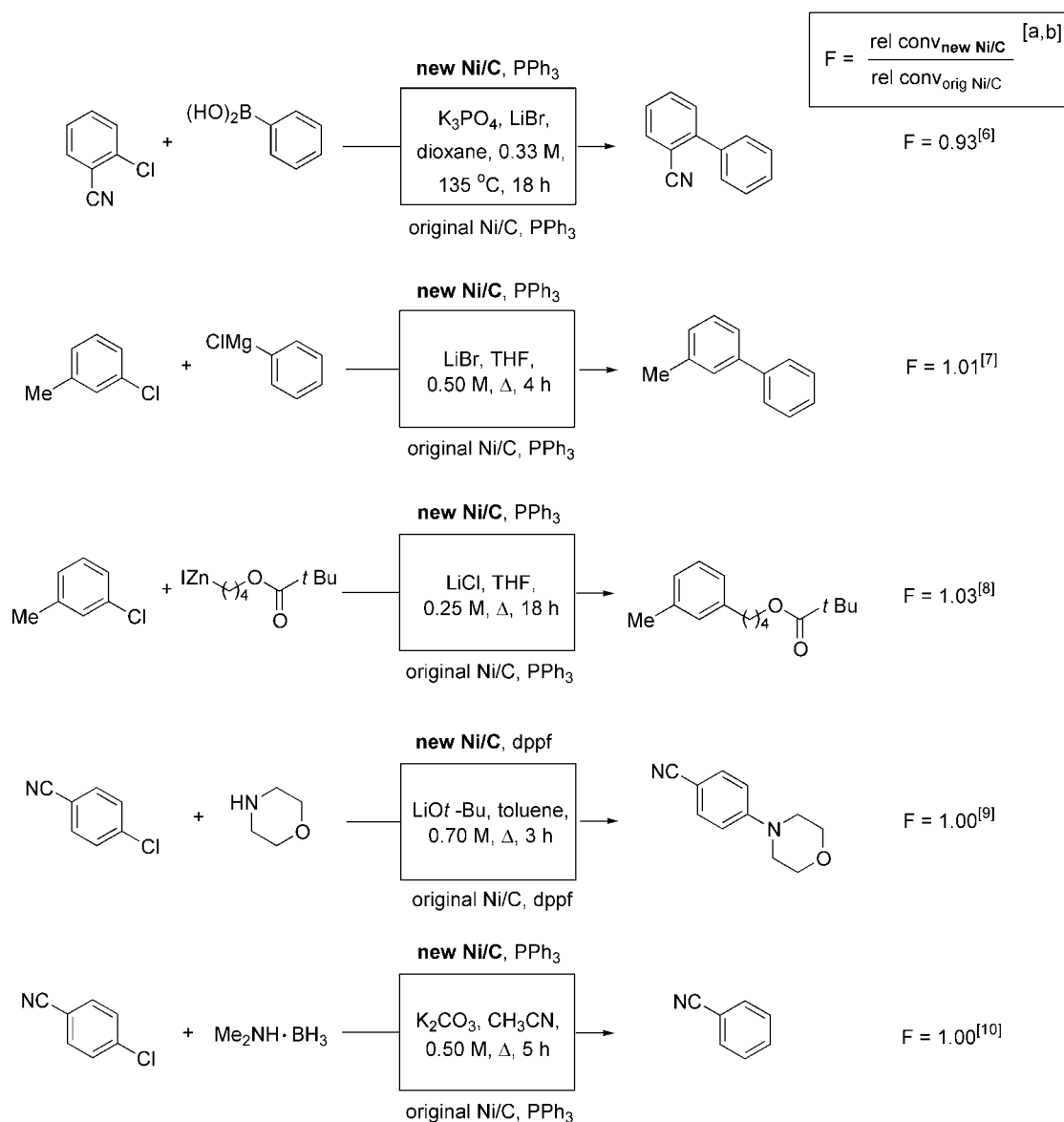
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In the procedure as originally developed,^[1] Ni(NO₃)₂ · 6H₂O was mixed with charcoal (Darco[®] KB-B, -100 mesh) in degassed water, with the slurry formed being heated to distill off the water. Once evaporated, the resulting material was treated with undistilled and degassed THF, the distillation of which led to Ni(II)/C which was washed again with additional water and finally more THF before drying under vacuum at 100 °C. In systematically modifying this procedure, it has been found that solvent degassing has no impact on catalyst activity. Importantly, it is no longer necessary to wash the Ni/C with THF, eliminating a distillation step as well as generation of organic waste. Thus, upon combining Ni(NO₃)₂ · 6H₂O and the charcoal in water, mixing under the influence of an ultrasonic bath at room temperature leads to essentially complete loading of the nickel salt

after a single distillation. Washing of the resulting Ni(II)/C with water returns, if any, only traces of Ni(NO₃)₂. After drying, the catalyst is ready for use. The more detailed temperature protocol used here should also afford Ni/C with greater regularity in particle sizes and metal distribution on the solid support.^[2,3]

To ensure catalyst activity, several side-by-side coupling reactions were conducted using Ni/C prepared by both the original and modified preparations. As illustrated in Scheme 1, all five examples afforded essentially identical results in terms of rates and extent of conversion (expressed in relative terms as 'F', which was ca. 1 in all cases). Catalyst derived from either Darco[®] activated carbon KB (-100 mesh) or KB-B (-100 mesh) showed no differences in subsequent coupling behavior.

Extraction of Ni/C prepared via this new procedure with either concentrated HCl or *aqua regia* led to samples for ICP analyses.^[4] The data indicate a loading which corresponds to 95% of the amount of nickel presumed to be mounted on the charcoal. The weight differential, presumably therefore, is attributable to water. It is known that Ni(NO₃)₂ · 6H₂O cannot be dried to completeness without decomposition.^[5,5] In our hands, heating this salt at 100–110 °C for 50 hours under vacuum, conditions which are *more* vigorous than those applied to our preparation of Ni(II)/C, lead to approximately one molecule of H₂O being retained in the crystal assuming no weight loss due to decomposition. The net implication from both of these observations (i.e., less nickel



[a] Reactions are unoptimized; relative conversions were measured by GC.

[b] For further details on these coupling reactions, see references [6-10].

Scheme 1. Comparison of activity between new and original Ni/C in side-by-side reactions, given as the quotient ‘F’ of their relative GC conversions.

having been mounted than calculated, and some water remaining on the solid support) is that they mitigate each others effect on the preparation and use of active Ni(0)/C. That is, the former would suggest less *n*-BuLi is needed to convert Ni(II)/C to the Ni(0) state, while the latter necessitates additional organolithium reagent for catalyst drying purposes. Thus, in practice, only in the case of Suzuki-like couplings was additional *n*-BuLi found to enhance the level of conversion (i.e., 4 equivalents versus 2 equivalents used for the other couplings), perhaps reflecting the need for additional hydroxide in the

medium. Control experiments using varying percentages of added LiOH should help to shed light on this particular aspect of these Ni/C-catalyzed couplings between an aryl chloride and a boronic acid.

In summary, a streamlined protocol has been developed for preparing Ni(II)/C. The advantages offered by this updated version include:

- either form of Darco® activated charcoal (KB or KB-B) may be used;
- deoxygenation of solvent is not required;
- pre-impregnation of nickel on the solid support via ultrasound leads to essentially complete load-

ing of the metal, and a likely better distribution of nickel particles;

- a single distillation of water from the initial mixing of the nickel(II) salt and charcoal is needed;
- no organic waste is generated in this process.

Ongoing work is aimed at determining the role of phosphines on the reactivity of Ni/C, as well as the potential for Ni(II) salts [other than Ni(NO₃)₂], which are less prone to retain water, to undergo impregnation on various forms of carbon.

Experimental Section

2nd Generation Procedure for Preparing Nickel(II)-on-Charcoal

A solution of Ni(NO₃)₂ · 6H₂O (Aldrich® 24,407-4, Ni content by ICP determination: 92%; 727 mg, 2.50 mmol) in deionized H₂O (75 mL) was added to 5.00 g Darco KB activated carbon, -100 mesh, 25% H₂O content, Aldrich 27-809-2 (or KB-B, -100 mesh, Aldrich 27,816-6). The flask was connected to an argon purged distillation setup and was treated in an ultrasonic bath under a positive argon flow for 30 min. The water was then distilled under an argon flow using a bath temperature of 175–180 °C. As the distillation ended, the pot temperature rises automatically but should be held below 210 °C for an additional 15 min. Upon cooling to rt, the black solid was washed with H₂O (2 × 50 mL) under argon, predried *in vacuo* at rt within the frit, and then dried *in vacuo* at 100 °C for 18 h. Using these specific amounts, all of the nickel is usually mounted on the support, which corresponds to 0.552 mmol Ni(II)/g catalyst, or 3.2% Ni/catalyst by weight.^[11]

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References and Notes

- [1] B. H. Lipshutz, *Adv. Synth. Catal.* **2001**, *343*, 313.
- [2] A. B. Stiles, *Catalyst Supports and Supported Catalysts*, Butterworth, Boston, **1987**, Chapter 5.
- [3] J. R. Anderson, *Structure of Metallic Catalysts*, Academic Press, New York, **1975**, Chapter 4.
- [4] (a) L. M. Gandia, M. Montes, *J. Catal.* **1994**, *145*, 276; in this publication, an EDTA/murexide titration was used to determine the exact Ni content; (b) *Inductively Coupled Plasma Mass Spectrometry* (Ed.: A. Montaser), Wiley-VCH, New York, **1998**.
- [5] (a) E. Bekyarova, D. Mehandjiev, *J. Colloid Interface Sci.* **1996**, *179*, 509; (b) G. D. Parkes, *Mellor's Modern Inorganic Chemistry*, John Wiley & Sons Inc., New York, **1967**, p. 938.
- [6] B. H. Lipshutz, J. A. Sclafani, P. A. Blomgren, *Tetrahedron* **2000**, *56*, 2139.
- [7] B. H. Lipshutz, T. Tomioka, P. A. Blomgren, J. A. Sclafani, *Inorg. Chim. Acta* **1999**, *296*, 164.
- [8] B. H. Lipshutz, P. A. Blomgren, *J. Am. Chem. Soc.* **1999**, *121*, 5819.
- [9] B. H. Lipshutz, H. Ueda, *Angew. Chem. Int. Ed.* **2000**, *39*, 4492.
- [10] B. H. Lipshutz, T. Tomioka, *Synlett*, in press.
- [11] From the filtrates of Suzuki and Kumada couplings, aqueous samples for ICP^[4b] analyses were prepared. These showed only traces of the nickel originally mounted on the charcoal had been lost from the solid support, the numbers being in agreement with those published previously.^[6,7]