Notes

Electrochemical Generation of Highly Reactive Nickel and Its Utilization for the Dehalogenative Coupling of Aryl Halides

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Summary: A highly reactive nickel like Rieke's nickel can be prepared by electrolysis of a DMF solution containing 0.3 M Bu_4NBF_4 in an undivided cell with a platinum cathode and a nickel anode without massive deposition onto the cathode at a constant current of 10 mA/cm^2 at 0 °C under an argon atmosphere. The transmission electron micrograph of the electrogenerated nickel shows the particle size to be 2−3 nm. The Ullmann-type reaction of aryl halides with the reactive nickel proceeded with approximately the same yields when using Rieke's metal.

Introduction

There are many reports on the methods of metal activation.[1] The typical examples of metal activation are Rieke's method,[2] the metal vaporization method,[3] metal−graphite reagent,[4] and the ultrasound method.[5] Each method has its own advantageous features. However, highly reactive metals have been generally prepared by the reduction of metal halides with lithium naphthalenide (Rieke's metal).[2,6,7] Other reductive methods for the preparation of highly reactive metals such as Reike's metal have not been reported. But, in many cases Rieke's method usually requires a long reaction time and complete removal of large amounts of naphthalene before or after the desired metal-induced reaction. For example, the preparation of active nickel using Rieke's method required stirring at room temperature for 12 h.

On the other hand, an electrochemical method for the preparation of reactive zinc has been reported.[8−11] The electrogenerated zinc was used for the oxidative addition reaction of allyl halides[8−10] and benzyl halides.[11] However, this electrogenerated zinc has not been used for the oxidative addition reaction of aromatic halides.

Although, Périchon and co-workers have recently been the first to report[12] the preparation of 3-thienylzinc bromide as an arylmetal reagent from 3-bromothiophene by an electrochemical method, this method is not similar to the preparation of active zinc, which is used for the oxidative addition of aryl halides, and requires electrolysis in the mixture of aryl halides and a supporting electrolyte. During the electrolysis, aryl halides, as a starting material, might be limited in use, because the aryl halides can possibility be oxidized or reduced by the electrolysis.

If the metals generated by the electrolysis have a high reactivity like Rieke's metal, this method would be considered to have a wide use in synthetic organic chemistry. Recently, Reetz and co-workers reported[13] the preparation of electrogenerated nickel, but the report was focused on the structural study of electrogenelated nickel and the reactivity for [3+2] cycloaddition reaction with the nickel as a catalyst. We now report a method for the preparation of a reactive nickel and the Ullmann-type reaction of aryl halides with the reactive nickel in order to demonstrate the high reactivity, as compared with Rieke's nickel. For general and wide use in synthetic organic chemistry, the nickel was prepared by electrolysis in an undivided cell at a constant current without potentiostatic control.

Results and Discussion

A highly reactive nickel was prepared by electrolysis in a DMF solution containing 0.3 M Bu_4NBF_4 using an undivided cell with a platinum cathode (1 × 2 cm) and a nickel anode (1 × 2 cm). Electrolysis was carried out without massive deposition on the cathode at a constant current of 10 mA/cm^2 at 0 °C under an argon atmosphere to give a nickel−DMF suspension. During the electrolysis, a nickel anode was dissolved to give nickel ions, which were reduced at the platinum cathode to give nickel metal. The nickel, electrolyzed at 0 °C, has

(1) Fiirstner, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 164.
(2) Rieke, R. D. *Science* **1989**, *246*, 1260.
(3) Kiindig, E. P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 292, and references therein.
(4) Savoia, D.; Trombini, C.; Umani-Ronchi, *A. Pure Appl. Chem.* **1985**, *57*, 1887.
(5) Einhorn, C.; Einhorn, J.; Luche, J. L.; *Synthesis* **1989**, 787.
(6) Ebert, G. W.; Rieke, R. D. *J. Org. Chem.* **1988**, *53*, 4482.
(7) Matsumoto, H.; Inaba, S.; Rieke, R. D. *J. Org. Chem.* **1983**, *48*, 840.
(8) Tokuda, M.; Miura, N.; Karasawa, T.; Fujita, H.; Suginome, H. *Tetrahedron Lett.* **1993**, *34*, 7607.
(9) Tokuda, M.; Kurono, N.; Mimura N. *Chem. Lett.* **1996**, 1091.
(10) Tokuda, M.; Satoh, S.; Suginome, H. *J. Org. Chem.* **1989**, *54*, 5608.
(11) Gosmin, C.; Rollin, Y.; Gebehenne, C.; Lojou, E.; Ratovelomanana, V.; Périchon, J. *Tetrahedron Lett.* **1994**, *35*, 5637.
(12) Gosmini, C.; Nédélec, J. Y.; Périchon, J. *Tetrahedron Lett.* **1997**, *38*, 1941.
(13) Reetz, M. T.; Breinbauer, R.; Wedemann, P.; Binger, P. *Tetrahedron* **1998**, *54*, 1233.

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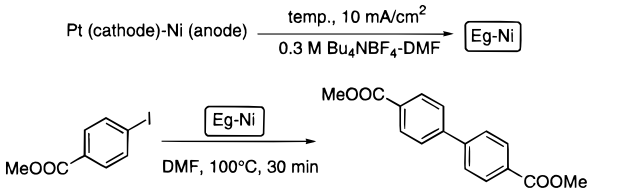
Table 1. Reaction of Ethyl 4-Iodobenzoate with Nickel Preparated at Various Temperatures



preparation of nickel temp (°C)	yield (%)
room temp	0
20	56
0	90
−20	41

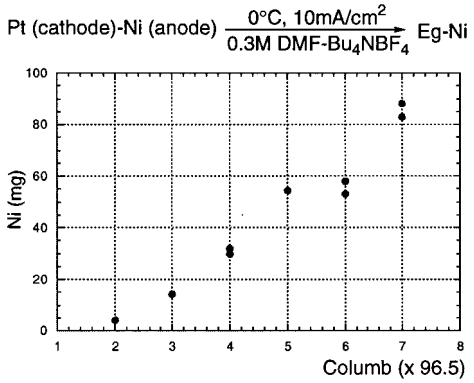


Figure 1. Amount of Eg-Ni powder against coulombs.

a high reactivity for an Ullman-type reaction. However, when the electrolysis was carried out at room temperature or −20 °C, the Ullmann-type reaction with the nickel produced low yields (Table 1).

First, the amount of nickel produced by electrolysis was investigated. As shown in Figure 1, 579 C (ca. 2 h) was needed for the generation of 1 mmol of nickel (59 mg). The electrolysis time depended on the electrode area.

One of the most important factors for the high reactivity of active metal is considered to be the particle size (or surface area).[14] Therefore, we investigated the particle size of the electrogenerated active nickel by transmission electron micrograph (TEM). The TEM shows the particle size to be 2−3 nm, as shown in Figure 2. These results show that the electrogenerated active nickel is the same size as Rieke's metals[14] and metal graphites.[15]

After the electrolysis, the nickel−DMF suspension was transferred to a reaction flask using a syringe and was used for the Ullmann-type reactions. As shown in Table 2, the reaction of various 4-substituted iodobenzenes with the nickel suspension (1.5 equiv of nickel for iodobenzenes based on Figure 1) proceeded to give the corresponding biphenyls in good yields. The reaction of 4-iodobenzonitrile and 4-iodoanisol with the electrogenerated nickel gave the corresponding biphenyls in 68% (Table 2, entry 4) and 75% (Table 2, entry 5) yields, respectively. The yields are almost the same, 85% and 68%, using Rieke's active nickel. On the other hand,

(14) Fiirstner, A. *Active Metals*; VHC: New York, 1995; pp 3, 437.
(15) Fiirstner, A.; Weidmann, H. *J. Chem. Soc., Dalton Trans.* **1988**, 2023.

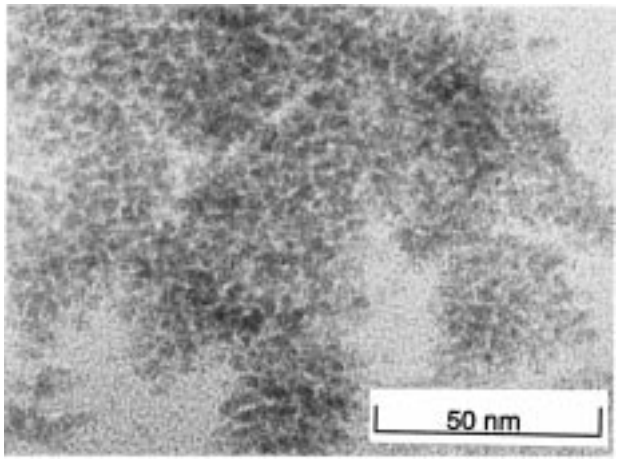
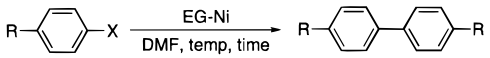


Figure 2. Transmission electron micrograph of electrogenerated nickel.

Table 2. Ullmann-Type Reaction with Aryl Halides



2

entry no.	X	R	temp (°C)	time (h)	yield (%)	**2**
1	I	COOMe	room temp	0.5	20	**a**
2	I	COOMe	50	0.5	60	**a**
3	I	COOMe	100	0.5	90	**a**
4	I	CN	100	1	68 (85)[a]	**b**
5	I	OMe	100	1	75 (68)[a]	**c**
6	I	H	100	1	58	**d**
7	I	NO_2	100	4	*b*	
8	Br	COOMe	100	6	5	**a**
9	Br	COOMe	130	6	37	**a**
10	Br	OMe	130	1	(0)[a]	
11	Br	CN	130	3	77 (71)[a]	**b**
12[c]	I	COOMe	100	24	0	

[a] Figures in parentheses are yields using Rieke's nickel. [b] Product is 4-iodoaniline (29%). [c] Yield using commercial available Ni (3−7 μm, 10 equiv).

the reaction using 10 equiv of commercially available nickel powder (3−7 μm) gave no corresponding biphenyl derivative (Table 2, entry 12).

Conclusion

The results of this work show that the nickel, which was prepared by electrolysis using Bu_4NBF_4 as the supporting electrolyte, has a high reactivity for Ullmann-type reaction, and TEM shows that the particle size of the active nickel is 2−3 nm. This method can be concluded to produce highly reactive nickel without using lithium naphthalenide, the preparation of which is somewhat complicated.

Experimental Section

All melting points and boiling points are uncorrected. The TEM was a JEOL JEM2000EXII with an acceleration voltage of 200 kV. The samples were under a nitrogen atmosphere. IR spectra were measured on a JASCO IR-810 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian Gemini 2000 (300 MHz). Chemical shifts are expressed in d (ppm) values with tetramethylsilane (TMS) as the internal reference, and coupling constants are expressed in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t

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= triplet, dd = double doublet, and dt = double triplet. Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on JMS-DX303 and JMS-AX500 instruments, respectively.

Preparation of Electrogenerated Nickel. A platinum sheet (1 × 2 cm^2) as the cathode and a nickel sheet (1 × 2 cm^2) as the anode were placed in a 15 mL H-shaped undivided cell which contained 0.3 M Bu_4NBF_4−DMF (8 mL). Electrolysis was carried out under an argon atmosphere at a constant current of 10 mA/cm^2 at 0 °C until 675 C of electricity was passed, producing a black suspension containing the active nickel (85 mg, 0.75 mmol based on Figure 1).

Construction of the Coulomb−Nickel Graph. After electrolysis, dry THF (30 mL) was added to the black nickel suspension, the mixture was centrifuged (3500 rpm, 1 h), and the supernatant was discarded. Dry THF was added to the precipite, the mixture was stirred and centrifuged (3500 rpm, 10 min), and the supernatant was discarded. The precipitate was then dried under reduced pressure.

General Procedure for the Ullmann-Type Reaction of Aryl Halides. The mixture of aryl halides (0.5 mmol) and elecrogenerated nickel was heated. After cooling, the reaction mixture was filtered through a Celite pad. The filtrate was extracted with Et_2O (30 mL × 3), dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography followed by distillation or recrystallization.

4,4′-Dimethoxycarbonylbiphenyl (2a): mp 204−206 °C (lit.[16] 208−212 °C); IR ν (neat) 1719, 1281 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.96 (6H, s), 7.70 (4H, d, J = 8.5 Hz), 7.80 (4H, d, J = 8.5 Hz).

4,4′-Dicyanobiphenyl (2b): mp 234−236 °C (lit.[17] mp 237−238 °C). IR ν (KBr) 2230 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.70 (4H, d, J = 8.5 Hz), 7.80 (4H, d, J = 8.5 Hz).

4,4′-Dimethoxybiphenyl (2c): mp 177−178 °C (lit.[16] mp 171−174 °C); IR ν (KBr) 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.85 (6H, s), 6.96 (4H, d, J = 8.5 Hz), 7.48 (4H, d, J = 8.5 Hz).

Biphenyl (2d): mp 68−69 °C (lit.[18] mp 71 °C); ^{1}H NMR ($CDCl_3$) δ 7.37 (2H, t, J = 6.9 Hz), 7.45 (4H, d, J = 6.9 Hz), 7.60 (4H, d, J = 6.9 Hz).

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(16) Ogliaruso, M. A.; Shadoff, L. A.; Becker, E. I. *J. Org. Chem*. **1963**, *28*, 2725.
(17) Kende, A. S.; Liebeskind, L. S.; Braitsch, D. M. *Tetrahedron Lett*. **1975**, *13*, 3775.
(18) Pouchert, C. J.; Behnke J. *The Aldrich Library of ^{13}C and ^{1}H FT-NMR Spectra 2*; Aldrich Chemical Commpany Inc.: New York, 1993; p 28.