



proceeded successfully with this reduction system (entry 3). Furthermore, this procedure showed remarkable selectivity to give the anilines without any further dehalogenation (entry 4, 5, 6, 10 and 11). The wide chemoselectivity of the reaction and the mild reaction conditions should be synthetically useful. After screening the reaction conditions, methanol has been found to be the most suitable solvent for the reaction in terms of reaction time and yield.<sup>13</sup> All the compounds obtained showed IR, NMR and mass spectral data compatible with the structure. Thus, we have been able to demonstrate the utility of easily accessible  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ /In system as a convenient reagent for effecting chemoselective reduction of nitroarenes. Although the role of nickel (II) chloride hexahydrate is still not clarified, it was assumed that reduction of nickel (II) chloride with indium provided low-valent nickel, which might be reducing the nitroarenes **1** to give the corresponding amines **2**. The reducing property exhibited by metal-metal salt combinations proceeds through transfer of one electron from the metal surface to the substrate. In such combinations elementary metal part needs to be more electropositive than the metal part of the salt.<sup>14</sup> Another important aspect of metal-metal salt combinations is the reduction potential difference of  $\text{Ni}^{+2}/\text{Ni}$  ( $E^0 = -0.236$  V),  $\text{In}^{+3}/\text{In}$  ( $E^0 = -0.338$  V) on which activity as well as reactivity of these reagents depend. We believe that the present procedure using  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ /In system proceeds through a single electron transfer (SET) process. The notable advantages of this methodology are mild reaction condition, readily available and inexpensive reagents, high yield, and tolerance of various functional groups.

In conclusion, we have demonstrated that this procedure using  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ /In system provides a useful alternative to the other presently used procedures since the reduction of aromatic nitro compounds proceeds expeditiously and in high yields under mild conditions. Further investigations of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ /In system as reducing agent in organic synthesis are currently in progress.

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## References

1. (a) For a review, see Tafesh, A. M.; Weiguny, J. *Chem. Rev.* **1996**, 96, 2035. (b) Mestoni, G.; Camus, A.; Zassinovich, G. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Reidel: Dordrecht, 1981; Vol. 4, pp 71-80.
2. Yoo, B. W.; Lee, S. J.; Yoo, B. S.; Choi, K. I.; Kim, J. H. *Synth. Commun.* **2002**, 32, 2489.
3. Nagaraja, D.; Pasha, M. A. *Tetrahedron Lett.* **1980**, 40, 7855.
4. Gohain, S.; Prajapati, D.; Sandhu, J. *Chem. Lett.* **1995**, 725.
5. Boothroyd, S.; Michael, A. *Tetrahedron Lett.* **1995**, 36, 2411.
6. Kumar, J. S.; Ho, M. M.; Toyokuni, T. *Tetrahedron Lett.* **2001**, 42, 5601.
7. Banik, B. K.; Mukhopadhyay, C.; Venkatraman, M. S.; Becker, F. *Tetrahedron Lett.* **1998**, 39, 7243.
8. Moody, C. J.; Pitts, M. R. *Synlett.* **1998**, 1028.
9. Bae, J. W.; Cho, Y. J.; Lee, S. H.; Yoon, C. M. *Tetrahedron Lett.* **2000**, 41, 175.
10. Lee, H. Y.; An, M. *Bull. Korean Chem. Soc.* **2004**, 25, 1717.
11. For review: (a) Nair, V.; Ros, S.; Jayan, C. N.; Pillia, B. S. *Tetrahedron* **2004**, 60, 1959. (b) Podlech, J.; Maier, T. C. *Synlett.* **2003**, 633. (c) Li, C.-J.; Chan, T.-H. *Tetrahedron* **1999**, 55, 11149.
12. (a) Yoo, B. W.; Choi, K. H.; Lee, S. J.; Yoon, C. M.; Kim, S. H.; Kim, J. H. *Synth. Commun.* **2002**, 32, 63. (b) Yoo, B. W.; Lee, S. J.; Yoo, B. S.; Choi, K. I.; Kim, J. H. *Synth. Commun.* **2002**, 32, 2489. (c) Yoo, B. W.; Choi, K. H.; Kim, D. Y.; Choi, K. I.; Kim, J. H. *Synth. Commun.* **2003**, 33, 53. (d) Yoo, B. W.; Hwang, S. K.; Kim, D. Y.; Choi, J. W.; Kang, S. O.; Yoo, B. S.; Choi, K. I.; Kim, J. H. *Bull. Korean Chem. Soc.* **2004**, 25, 1633. (e) Choi, K. H.; Choi, K. I.; Kim, J. H.; Yoon, C. M.; Yoo, B. W. *Bull. Korean Chem. Soc.* **2005**, 26, 1495. (f) Han, J. H.; Choi, J. W.; Choi, K. I.; Kim, J. H.; Yoo, B. W. *Bull. Korean Chem. Soc.* **2005**, 26, 1921.
13. Sonication were carried out in a BRANSONIC ultrasonic cleaner bath, which delivered a 47 kHz wave, with a fixed electrical power of 125 Watts.
14. A typical procedure for the reaction: Nickel(II) chloride hexahydrate (238 mg, 1.0 mmol), indium powder (512 mg, 4.0 mmol) and MeOH (4 mL) were mixed and the resulting mixture was stirred at room temperature under sonication for 30 min. A dark-yellow solution of the complex was obtained. Nitrobenzene (123 mg, 1.0 mmol) was added to this solution and the reaction mixture was stirred for 1.5 hr at room temperature. The solvent was evaporated under reduced pressure and the residue was extracted with ether. The extract was washed with brine, dried over anhydrous  $\text{MgSO}_4$ . The crude product was purified by silica gel column chromatography (hexane : ethyl acetate = 6 : 1) to afford aniline (88 mg, 95%).
15. Mourad, M. S.; Verma, R. S.; Kabalka, G. W. *J. Org. Chem.* **1985**, 50, 133.