Reversible Chemisorption of CO at Room Temperature on Ni(0) Complexes

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Carbon monoxide (CO) is a key C1 source for many chemicals, including alcohols, acetic acid, and copolymers comprising CO and olefins. The development of an effective method for the separation/purification of CO is valuable, especially when the method can be conducted under less energy-consuming conditions. As such a procedure to separate/purify CO, the reversible chemisorption of CO has been exclusively studied using higher-valent metal complexes.[1)] However, in general, a temperature higher than that used in the adsorption process was required to achieve an efficient desorption process. Herein, we report a room-temperature chemisorption of CO using the interconversion between zero-valent nickel di- and tri-carbonyl complexes bearing *N*-phosphine oxide-substituted imidazolinylidene[2)], which can be driven only by the change of the pressure.

Treatment of a THF solution of **1** and $Ni(cod)_2$ with 2.2 equivalents of CO afforded (κ-*C*,*O*-**1**)$Ni(CO)_2$ (**2**) in 93% yield (Figure 1a). On the other hand, the reaction using 8.0 equivalents of CO in toluene furnished (κ-*C*-**1**)$Ni(CO)_3$ (**3**) in 82% yield. Stirring a crystalline powder of **3** under the reduced pressure for 10 h resulted in the formation of **2** in 50% yield (Figure 1b). To improve the efficiency, imidazolium-based ionic liquid (**IL**) was used as a dispersant for **3**, resulting in the formation of **2** in 97% yield. Stirring **2** with **IL** in the presence of CO (1 atm) at room temperature afforded **3** in 98% yield within 15 min.

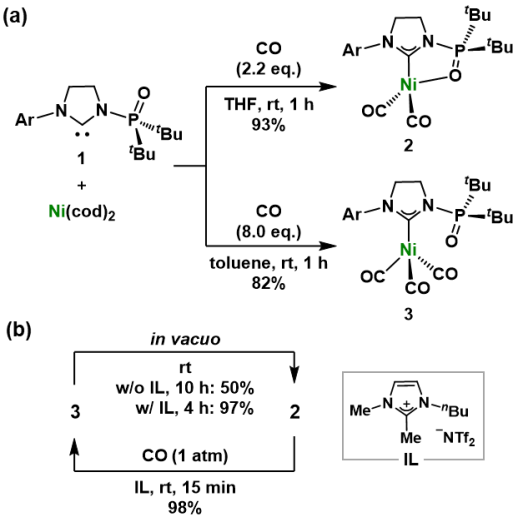

Figure 1. (a) Synthesis of **2** and **3** (Ar = 2,6-diisopropylphenyl). (b) Chemisorption of CO with **2**/**3**.

1) For examples, see: a) D. Benito-Garagorri, M. Puchberger, K. Mereiter, K. Kirchner, *Angew. Chem. Int. Ed.* **2008**, *47*, 9142. b) H. Sato, W. Kosaka, R. Matsuda, A. Hori, Y. Hijikata, R. V. Belosludov, S. Sakaki, M. Takata, S. Kitagawa, *Science* **2014**, *343*, 167. 2) Y. Hoshimoto, S. Ogoshi, *Bull. Chem. Soc. Jpn.* **2021**, *94*, 327.