

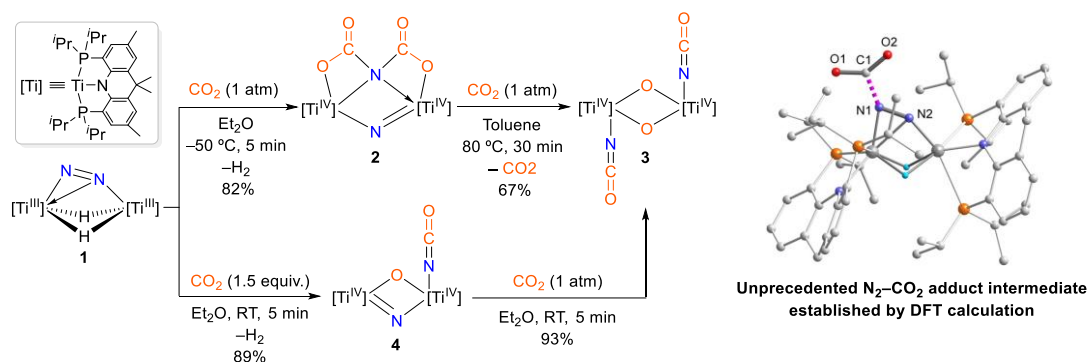
Dinitrogen Cleavage and Functionalization by Carbon Dioxide at a Ditunganium Dihydride Framework

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Dinitrogen (N₂) and carbon dioxide (CO₂) are among the most inert molecules. The coupling of these two molecules through N–C bond formation and N–N and C–O bond cleavage is highly challenging and has not been reported previously.¹ We report here the reaction of a well-defined dinitrogen dititanium hydride complex (**1**)² with CO₂, which involved not only N–C bond formation but also N–N and C–O bond cleavage (Scheme 1). Exposure of the dinitrogen dititanium hydride complex **1** with CO₂ (1 atm) at –50 °C selectively yielded a nitrido/*N,N*-dicarboxylated-amido complex **2** through N₂ cleavage and dicarboxylation at one nitrogen atom. When **1** was mixed with 1.5 equiv of CO₂ at room temperature, a nitrido/oxo/isocyanate complex **4** was formed through N₂ cleavage, CO₂ partial deoxygenation and N=C double bond formation. The reaction of **4** with CO₂ (1 atm) at room temperature yielded the diisocyanate complex **3**. While **2** did not react with CO₂ at room temperature, it was converted to **3** under 1 atm CO₂ at 80 °C. Computational studies revealed that the reaction was initiated by the nucleophilic attack of the N₂ unit in **1** to CO₂.

Scheme 1



- 1) Previous studies on the reaction of N₂ with CO₂ without N–N and C–O bond cleavage: a) W. H. Bernskoetter, E. Lobkovsky, P. J. Chirik, *Angew. Chem., Int. Ed.* **2007**, *46*, 2858. b) D. J. Knobloch, H. E. Toomey, P. J. Chirik, *J. Am. Chem. Soc.* **2008**, *130*, 4248. c) Y. Nakanishi, Y. Ishida, H. Kawaguchi, *Angew. Chem., Int. Ed.* **2017**, *56*, 9193.
- 2) Z. Mo, T. Shima, Z. Hou, *Angew. Chem., Int. Ed.* **2020**, *59*, 8635.