Mechanistic Study of BPh_3-Catalyzed *N*-Methylation of Amines with CO_2 and Phenylsilane

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Abstract

BPh_3 was found to catalyze the highly selective *N*-methylation of secondary amines at 30 ^{0}C with CO_2 (1 atm) and $PhSiH_3$ under solvent-free conditions [**1**]. In the present work, we have clarified the mechanism of BPh_3-catalyzed *N*-methylation of *N*-methylaniline with CO_2 and $PhSiH_3$ using the DFT calculations at ωB97XD/6-31G(d), 6-31++G(d,p) for the hydride of $PhSiH_3$ level of theory [**2**]. The DFT results revealed that the BPh_3 promotes the conversion of *N*-methylaniline and CO_2 substrates into a zwitterionic carbamate to give three-component species $[Ph(Me)(H)N^+CO_2^-\cdots BPh_3]$. The carbamate and BPh_3 act as the nucleophile and Lewis acid, respectively, for the cooperative activation of $PhSiH_3$ to generate borohydride $[HBPh_3]^-$ species, which catalyzes the reduction of CO_2 to form key reactive species such as silyl formats, bis(silyl)acetals, and formaldehyde. These key CO_2-derived reactive species are essential for *N*-methylation reaction. In addition, we realized that a water molecule might act as a nucleophile to activate $PhSiH_3$. Hence, we have explored other mechanisms and suggested hypothetical water-assisted mechanisms for the generation of active $[HBPh_3]^-$ species. Our results indicate that $[HBPh_3]^-$ species can be generated relatively easily by the involvement of water. Interestingly, we have found that if acetonitrile is used as a solvent, acetonitrile can serve as a Lewis base to weakly activate carbonic acid or water, both of which can attack the silicon atom of $PhSiH_3$. The elucidation of this catalytic mechanism will be useful for the further progress of CO_2 fixation chemistry in future and development of new catalysts and reactions.

References

[**1**] Murata, T.; Hiyoshi, M.; Maekawa, S.; Saiki, Y.; **Ratanasak, M.;** Hasegawa, J.; Ema, T.*, Deoxygenative CO_2 Conversions with Triphenylborane and Phenylsilane in the Presence of Secondary Amines or Nitrogen-Containing Aromatics. *Green Chem.* **2022,** *24* (6), 2385-2390.

[**2**] **Ratanasak, M.;** Murata, T.; Adachi, T.; Hasegawa, J.*; Ema. T.*, Mechanism of BPh_3-Catalyzed *N*-Methylation of Amines with CO_2 and Phenylsilane: Cooperative Activation of Hydrosilane. *Chem. Eur. J.* **2022**, e202202210 (Selected as Inside Front Cover & Selected as a Hot Paper).