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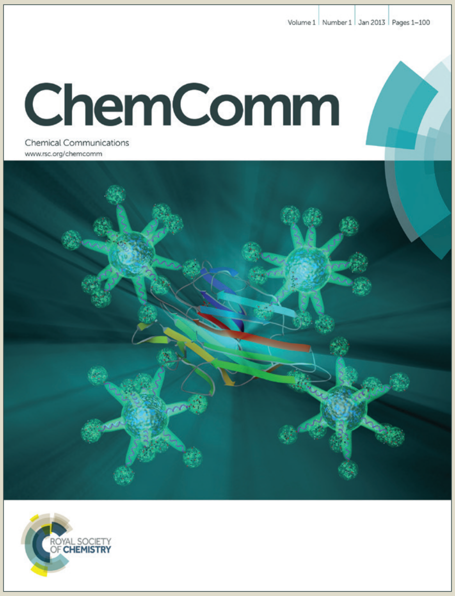

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ARTICLE TYPE

The Crucial Roles of $MgCl_2$ as a Non-innocent Additive in the Ni-Catalyzed Carboxylation of Benzyl Halide with CO_2

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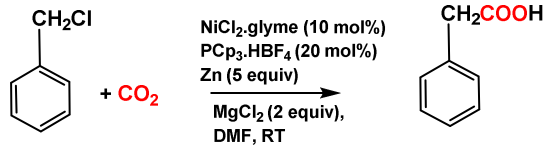
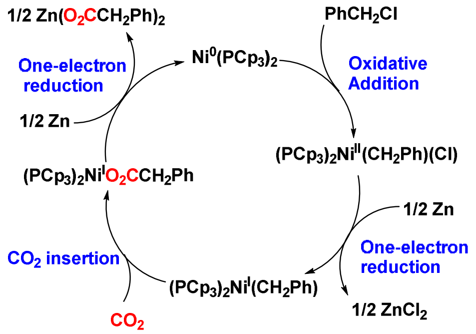
Ni-catalyzed carboxylation of the C(sp^3)-Cl bond with CO_2 in the presence of $MgCl_2$ was theoretically investigated. $MgCl_2$ plays three crucial roles to stabilize a Ni^I-CO_2 adduct and accelerate the CO_2 insertion as a non-innocent additive and one-electron reduction process as one kind of reagent.

The transformation of CO_2 into useful chemicals has been one of the important topics in the last decade.[1] In this regard, various attempts have been made using transition-metal complexes as catalyst for the CO_2 transformation.[2] Among those efforts, direct carboxylation of organic halide with CO_2 is in particular attractive because of the importance of carboxylic acid in various applications.[3] However, the reports of such direct carboxylation have been elusive except for several pioneering works by Martin group[4] and Tsuji group.[5] Correa and Martin succeeded to transform aryl bromides to the carboxylic acids with CO_2 using a Pd catalyst.[4] Tsuji group successfully transformed aryl chloride to carboxylic acids with CO_2, using a Ni^0 catalyst.[5] This report is the first example that shows the utilization of an unusual Ni^I intermediate in the catalytic cycle of a metal-catalyzed CO_2 fixation. In those reports,[4,5] the direct carboxylation of the C(sp^2)-X (X = Br or Cl) bond was successfully performed but that of the C(sp^3)-X bond was not. In general, the C(sp^3)-X bond is less reactive than the C(sp^2)-X bond.[6] Interestingly, Martin and co-workers succeeded the transformation of the C(sp^3)-Cl bond of benzyl halide to phenylacetic acid with CO_2 using a Ni catalyst, very recently (Scheme 1).[7] This Ni-catalytic system contains Zn powder and $MgCl_2$. If Zn powder is absent, no catalytic conversion occurs. If $MgCl_2$ is not added, the yield is very low. The experimentally proposed reaction mechanism suggests that a Ni^I intermediate might be crucial in the catalytic cycle, as shown in Scheme 2. However, mysterious is the role of $MgCl_2$; it is not clear at all what roles $MgCl_2$ plays in this catalytic carboxylation to provide good yield of the product.

Herein, we theoretically investigated this Ni-catalyzed carboxylation of benzyl chloride to phenylacetic acid in the presence of $MgCl_2$. Our main purpose is to elucidate what roles $MgCl_2$ plays in this catalytic reaction. All the calculations were carried out with the B3LYP-D functional; see supporting information (ESI) for computational details. The Gibbs activation energy ($\Delta G^{o\ddagger}$) is defined as an energy difference between the transition state (TS) and the corresponding precursor complex or reactant.



Scheme 1. Ni-catalyzed carboxylation of $PhCH_2Cl$ with CO_2.[7]



Scheme 2. Plausible mechanism for the Ni-catalyzed carboxylation reaction of $PhCH_2Cl$ with CO_2.

We investigated first the catalytic reaction in the absence of $MgCl_2$. As suggested experimentally[5a,7] and shown theoretically,[5b] it is likely that the first step of the catalytic cycle is the oxidative addition of benzyl chloride **1** to $Ni(PCp_3)_2$ **2** (Cp = cyclopentyl); see scheme 2. In this reaction, **1** interacts with **2** to form a Ni^0 complex of benzyl chloride $Ni(\eta^2\text{-}PhCH_2Cl)(PCp_3)_2$ **3** in which the phenyl group coordinates with the Ni-center in an η^2-mode (Fig. 1). The similar precursor complexes were theoretically reported.[8] Starting from **3**, the oxidative addition of the C(sp^3)-Cl bond occurs to afford a four-coordinate Ni^{II}-intermediate *cis*-$Ni^{II}(Cl)(CH_2Ph)(PCp_3)_2$ **4** via a transition state **$TS_{3\text{-}4}$**. The $\Delta G^{o\ddagger}$ is 9.3 kcal/mol, indicating that the oxidative addition easily occurs (Fig 1). The complex **4** isomerizes to a more stable trans-form $Ni^{II}(Cl)(CH_2Ph)(PCp_3)_2$ **5** (see ESI).

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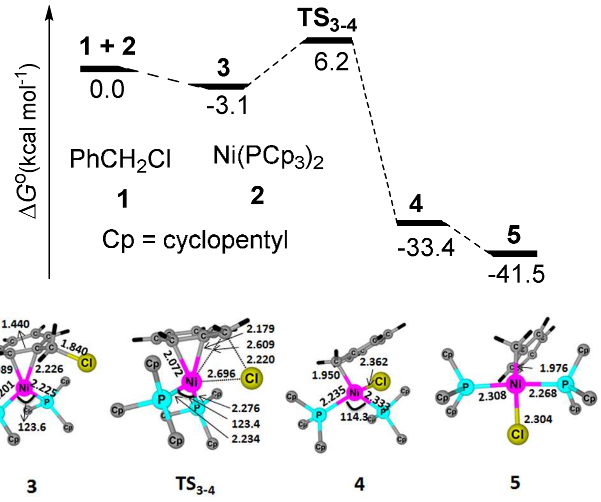

Fig. 1 Changes in the Gibbs energy and geometry in the oxidative addition of 1 to 2. Cp represent a cyclopentyl group. Bond lengths are in Å and angles in degree.

The next step is either one-electron reduction of **5** to generate a Ni^I intermediate or direct CO_2 insertion into the Ni^{II}-CH_2Ph bond of **5**. As shown in Fig. 2, the $\Delta G^{\circ\ddagger}$ for the CO_2 insertion is 41.7 kcal/mol, indicating that the direct CO_2 insertion is unlikely. Thus, **5** must undergo one-electron reduction by Zn to generate a Ni^I species $Ni^I(CH_2Ph)(PCp_3)_2$ **7**. The Gibbs energy change ($\Delta G_1°$) for this one-electron reduction (eqn (1)) is -18.5 kcal/mol, indicating that this process easily occurs. Further one-electron reduction of **7** to **2** is difficult because the $\Delta G_{S3}°$ value is 1.3 kcal/mol (see eqn (S3) in ESI).

$$\tfrac{1}{2}\,\text{Zn} + \mathbf{5} + \text{DMF} \rightarrow \tfrac{1}{2}\,\text{ZnCl}_2(\text{DMF})_2 + \mathbf{7} \qquad (1)$$

In the next step, CO_2 coordinates with the Ni-center of **7** to form an η^1-CO_2 complex $Ni(CH_2Ph)(PCp_3)_2(\eta^1\text{-}CO_2)$ **8** (Fig. 3). Then, the CO_2 is inserted into the Ni^I-CH_2Ph bond to afford a Ni^I-phenylacetate complex $Ni(\eta^1\text{-}OCOCH_2Ph)(PCp_3)_2$ **9** via a four-member transition state $\mathbf{TS_{8\text{-}9}}$. The $\Delta G^{\circ\ddagger}$ value is 8.6 kcal/mol relative to **7**, indicating that the CO_2 insertion into the Ni^I-CH_2Ph bond occurs much more easily than into the Ni^{II}-CH_2Ph bond (Fig 2). The final step is the one-electron reduction of **9** with Zn. The negative $\Delta G_2°$ value (-5.2 kcal/mol) of this one-electron reduction indicates that this reaction can occur; see eqn (S4) in ESI. Based on these results, it is concluded that even in the absence of $MgCl_2$, benzyl chloride is transformed to phenylacetic acid, which is in accord with the experimental result that the direct carboxylation of benzyl chloride occurs with a poor yield in the absence of $MgCl_2$.

Next, we investigated the catalytic reaction in the presence of $MgCl_2$. It is likely that $MgCl_2$ does not participate in oxidative addition. The next step is the CO_2 insertion. Though a Ni^{II}-CO_2 adduct could not be optimized in the absence of $MgCl_2$, a Ni^{II}-η^1-CO_2 adduct $NiCl(CH_2Ph)(PCp_3)_2{\cdot}MgCl_2$ **10** was optimized, as shown in Fig. 2. This is probably because $MgCl_2$ stabilizes the CO_2 coordinate bond with the Ni^{II} center. However, **10** is considerably less stable than **5** by 15.2 kcal/mol (Fig. 2). Also, the CO_2 insertion needs a very large $\Delta G^{\circ\ddagger}$. Hence, one-electron reduction of **5** to **7** must occur even in the presence of $MgCl_2$.

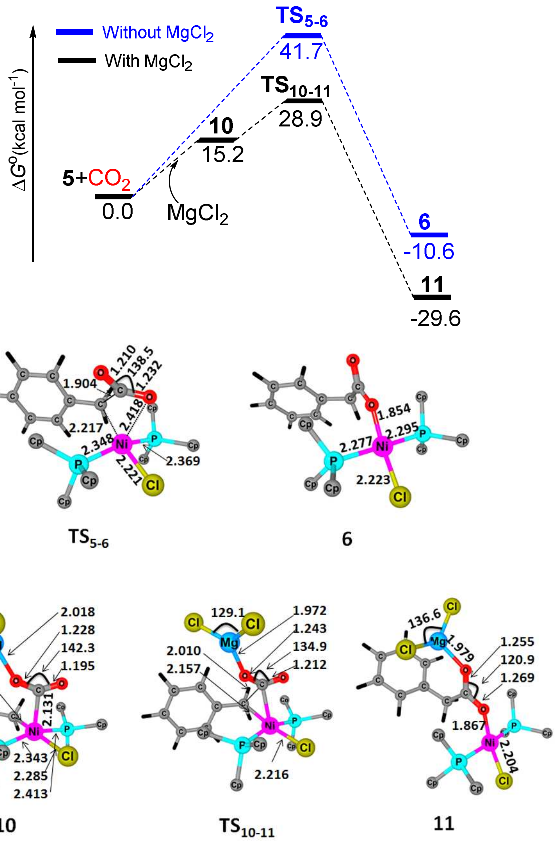

Fig. 2 Changes in the Gibbs energy and geometry in the CO_2 insertion into the Ni^{II}-CH_2Ph bond of **5**. Cp represents a cyclopentyl ligand. All the bond lengths are in Å and angles are in degree.

In the presence of CO_2 and $MgCl_2$, **7** coordinates with CO_2 and $MgCl_2$ to afford an adduct $Ni(CH_2Ph)(PCp_3)_2(\eta^1\text{-}CO_2)(MgCl_2)$ **12** (Fig. 3). The Mg-O distance (1.951 Å) and the O-C-O angle (133.6°) in **12** are smaller than in **10**. Also, the Ni-C distance (1.957 Å) and the O-C-O angle are considerably smaller than in **8** without $MgCl_2$. These geometrical features indicate that the Mg-O and Ni-CO_2 interactions are considerably stronger in **12** than in **8**. Consistent with this geometry, the ΔG° is -14.0 kcal/mol relative to **8**. Starting from **12**, the CO_2 is easily inserted into the Ni^I-CH_2Ph bond via a transition state $\mathbf{TS_{12\text{-}13}}$ to afford a Ni^I-(η^1-phenylacetate)-$MgCl_2$ adduct **13** (Fig. 3). It should be noted that $\mathbf{TS_{12\text{-}13}}$ exists considerably below $\mathbf{TS_{8\text{-}9}}$ by 12.0 kcal/mol, which is enough to accelerate very much the CO_2 insertion. In the DMF solvent, DMF coordinates with $MgCl_2$ to afford $MgCl_2(DMF)_4$. We investigated $\mathbf{TS_{12\text{-}13}}$ interacting with $MgCl_2(DMF)_3$, in which one DMF dissociates from the Mg centre because the Mg interacts with the O of CO_2: remember that Mg^{2+} is six-coordinate. When such coordination is considered, $\mathbf{TS_{12\text{-}13}}$ is more stable than $\mathbf{TS_{8\text{-}9}}$ by 7.6 kcal/mol and the $\Delta G^{\circ\ddagger}$ is 1.0 kcal/mol relative to **7** + CO_2 + $MgCl_2(DMF)_4$; see page S10 in SI for details. Based on these results, it is concluded that $MgCl_2$ accelerates the CO_2 insertion into the Ni^I-CH_2Ph bond as a non-innocent additive. This is the first theoretical finding showing that $MgCl_2$ accelerates the CO_2 insertion.

Recently, Knochel group[9] experimentally observed that $MgCl_2$ accelerates CO_2 insertion into an arylzinc bond but the reason was not discussed. It is of considerable interest to understand the reason for the acceleration of CO_2 insertion by $MgCl_2$. It should be noted that the electron population of CO_2 is much larger and those of the Ni and benzyl moieties are much smaller in **12** than in **7** (see Fig. S4).[10] These results clearly show that $MgCl_2$ enhances the charge transfer from the Ni-CH_2Ph moiety to the CO_2 moiety. This is because the electrostatic interaction between the positively charged Mg atom and the negatively charged O atom of CO_2 stabilizes the π* orbital energy of CO_2. As the CO_2 insertion proceeds, the electron population of the CH_2Ph moiety moderately decreases but that of the CO_2 moiety moderately increases. These changes are much smaller than those in the absence of $MgCl_2$. Hence, it is concluded that the CO_2 moiety has already enough electron population in **12** and thereby the electronic structure does not need to change very much in the CO_2 insertion in the presence of $MgCl_2$. Also, the Ni^I-O bond energy of **13** is considerably larger than that of **9** by 19.3 kcal/mol. These results indicate that the CO_2 insertion is kinetically and thermodynamically favoured by the interaction with $MgCl_2$.

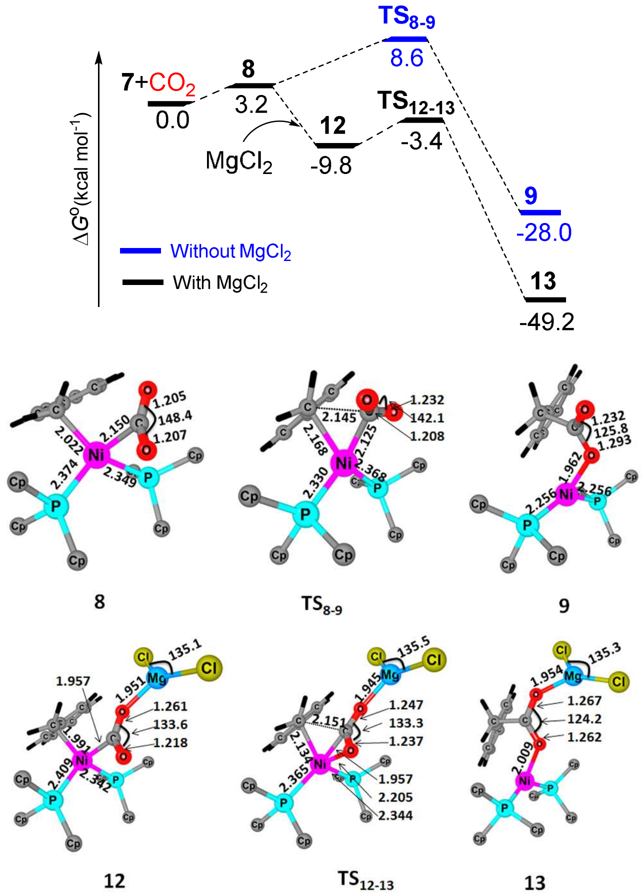

Fig. 3 Changes in the Gibbs energy and geometry in the CO_2 insertion into the Ni^I-CH_2Ph bond of **7**. Cp represents a cyclopentyl ligand. All the bond lengths in Å and angles are in degree.

The final step is the one-electron reduction of **13** with Zn. The calculated $\Delta G_{S5}{}^0$ value for this step is -12.4 kcal/mol (eqn. (S5)). The anion exchange between $Zn(O_2CCH_2Ph)_2$ and $MgCl_2$ occurs with a considerably negative $\Delta G_{S6}{}^0$ of -15.4 kcal/mol, indicating that the formation of $Mg(O_2CCH_2Ph)_2$ is thermodynamically more favourable (eqn. (S6)). These results suggest that $MgCl_2$ also assists the one-electron reduction as a reagent. Because $MgCl_2$ is consumed in the reaction, two-equivalent of $MgCl_2$ to benzyl chloride is necessary (Scheme 1).[7] Gong group[11] recently reported that $MgCl_2$ accelerates the reductive coupling between alkyl iodides and aryl acid chlorides probably because $MgCl_2$ activates Zn-powder. However, it is shown here that $MgCl_2$ accelerates one-electron reduction by anion-exchange, which is a new mechanism.

In conclusion, the Gibbs free energy profile for the total catalytic cycle (Fig. S5) clearly indicates that $MgCl_2$ promotes the carboxylation of benzyl chloride with CO_2. Based on the computational results, we disclosed here that $MgCl_2$ stabilizes the Ni^I-CO_2 adduct and accelerates the CO_2 insertion as a non-innocent additive and one-electron reduction as one reagent. To the best of our knowledge, this is the first report that shows the unprecedented roles of $MgCl_2$. The knowledge of the interplay between the metal catalysis and non-innocent additives is crucial for new development in catalytic reactions by transition metal complexes. Further study is needed about this reaction, on which theoretical study is under progress.

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REFERENCES

(1) (a) X. Xiaoding and J. A. Moulijn. *Energy & Fuels* 1996, **10**, 305; (b) D. J. Darensbourg. *Chem. Rev.* 2007, **107**, 2388; (c) S. Solomon, G. K. Plattner, R. Knutti and P. Friedlingstein. *Proc. Natl. Acad. Sci. U. S. A.* 2009, **106**, 1704; (d) S. N. Riduan and Y. Zhang. *Dalton. Trans.* 2010, **39**, 3347; (e) M. Mikkelsen, M. Jørgensen and F. C. Krebs. *Energy Environ. Sci.* 2010, **3**, 43; (f) T. Fan, X. Chen and Z. Lin. *Chem. Commun.* 2012, **48**, 10808; (g) Y. Tsuji and T. Fujihara. *Chem. Commun.* 2012, **48**, 9956.
(2) (a) T. Sakakura, J. C. Choi and H. Yasuda. *Chem. Rev.* 2007, **107**, 2365; (b) C. S. Yeung and V. M. Dong. *J. Am. Chem. Soc.* 2008, **130**, 7826; (c) K. Kobayashi and Y. Kondo. *Org. Lett.* 2009, **11**, 2035; (d) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann and F. E. Kühn. *Angew. Chem. Int. Ed.* 2011, **50**, 8510; (e) M. Aresta, A. Dibenedetto and A. Angelini. *Chem. Rev.* 2014, **114**, 1709.
(3) (a) L. J. Gooßen, N. Rodríguez and K. Gooßen. *Angew. Chem. Int. Ed.* 2008, **47**, 3100; (b) X. Cai and B. Xie. *Synthesis* 2013, **45**, 3305.
(4) A. Correa and R. Martín. *J. Am. Chem. Soc.* 2009, **131**, 15974.
(5) (a) T. Fujihara, K. Nogi, T. Xu, J. Terao and Y. Tsuji. *J. Am. Chem. Soc.* 2012, **134**, 9106; (b) F. B. Sayyed, Y. Tsuji and S. Sakaki. *Chem. Commun.* 2013, **49**, 10715.
(6) (a) A. Ariafard and Z. Lin. *Organometallics* 2006, **25**, 4030; (b) N. Kambe, T. Iwasaki and J. Terao. *Chem. Soc. Rev.* 2011, **40**, 4937.
(7) T. León, A. Correa and R. Martin. *J. Am. Chem. Soc.* 2013, **135**, 1221.
(8) (a) Y. Y. Ohnishi, Y. Nakao, H. Sato, Y. Nakao, H. Hiyama and S. Sakaki. *Organometallics* 2009, **28**, 2583; (b) W. Guan, F. B. Sayyed, G. Zeng and S. Sakaki. *Inorg. Chem.* 2014, DOI: 10.1021/ic5003429.
(9) A. Metzger, S. Bernhardt, G. Manolikakes and P. Knochel. *Angew. Chem. Int. Ed.* 2010, **49**, 4665.
(10) (a) S. Sakaki, K. Kitaura and K. Morokuma. *Inorg. Chem.* 1982, **21**, 760; (b) S. Sakaki, K. Kitaura, K. Morokuma and K. Ohkubo. *Inorg. Chem.* 1983, **22**, 104; (c) S. Sakaki. *J. Am. Chem. Soc.* 1990, **112**, 7813; (d) Y. Musashi and S. Sakaki. *J. Am. Chem. Soc.* 2002, **124**, 7588.
(11) F. Wu, W. Lu, Q. Qian, Q. Ren and H. Gong. *Org. Lett.* 2012, **14**, 3044.