ChemComm

COMMUNICATION

The crucial role of a Ni(I) intermediate in Ni-catalyzed carboxylation of aryl chloride with CO_2: a theoretical study†

Fareed Bhasha Sayyed,[a] Yasushi Tsuji[b] and Shigeyoshi Sakaki*[a]

In Ni(0)-catalyzed carboxylation reaction of aryl chloride with CO_2, the formation of a Ni(I) species is crucial, because the CO_2 insertion into the Ni(I)–Ph bond easily occurs but that into the Ni(II)–Ph bond cannot. This is a key point of this successful carboxylation reaction.

Over the past few years, significantly large growth has been achieved in CO_2 conversion to useful chemicals with catalysts.[1,2] Transition metal complexes are promising catalysts for the CO_2 conversion. Actually, many catalysts have been developed for the syntheses of a variety of useful chemicals.[3] In particular, syntheses of carboxylic acids and their derivatives from CO_2 are of recent interest because they are important starting materials of organic syntheses.[4] For instance, carboxylation reactions of arylzinc[5] and various organic substrates involving N–H,[6] aryl C–H,[6,7] alkene C–H[8] and alkyne C–H[9] bonds have been well established. However, the carboxylation of aryl halides has remained elusive.[10] Correa and Martin proposed Pd-catalyzed direct carboxylation reaction of aryl bromides with CO_2.[11] However, this reaction can occur only when reactive aryl bromides are employed but cannot when aryl chlorides are employed. Very recently, Tsuji *et al.* succeeded in overcoming this limitation by developing a nickel catalytic system. As shown in Scheme 1, aryl chloride is directly transformed to the corresponding carboxylic acid with CO_2 in the presence of a Ni-complex and Mn–Et_4NI.[12] Experimental observations suggest that some Ni(I) intermediate participates in the catalytic cycle. Later a similar carboxylation reaction of benzyl chloride has been reported by Martin and his co-workers.[13] No catalytic cycle including Ni(I) species has yet been established; only a few limited proposals have been presented without any evidence.[14]

In this context, several questions naturally arise: which Ni(I) species participates in the reaction? Why is Ni(I) species necessary? And, which elementary step is accelerated by the Ni(I) species?
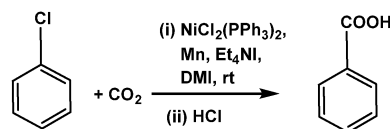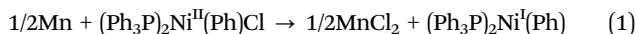

Scheme 1 Ni-catalyzed carboxylation of PhCl with CO_2 (ref. 12).

It is of considerable importance to elucidate whether the mechanism including Ni(I) species is correct or not.

In this work, we theoretically investigated this reaction to elucidate the total catalytic cycle and to provide a good understanding about it. All the calculations were carried out by the DFT method with the B3LYP-D functional,[15] where Gaussian 09 package was employed.[16] The Gibbs activation energy ($\Delta G^{0\neq}$) is defined as the difference in the Gibbs energy between the transition state (TS) and its corresponding precursor complex.

Scheme 2 shows the plausible mechanism.[17] The reaction starts with the oxidative addition of phenyl chloride to Ni(PPh_3)_2. Coordination of phenyl chloride leads to the formation of an η^2-coordinate Ni(PPh_3)_2(C_6H_5Cl) **3**; see Fig. 1. Starting from **3**, the C–Cl bond cleavage occurs through a three-member transition state **TS_{3-4}** to afford a *cis*-nickel(II) chlorophenyl complex, *cis*-NiCl(Ph)(PPh_3)_2 **4**. Complex **4** can isomerize to a more stable square planar *trans*-form **5**; see ESI,† page S3, for this isomerization. $\Delta G^{0\neq}$ for the oxidative addition is 6.2 kcal mol^{-1}, indicating that this is an easy process.

Because **4** and **5** are Ni(II) complexes, they can undergo one electron reduction by Mn. The reduction process is represented using eqn (1).[18] The Gibbs energy change (ΔG_1^0) is -25.4 kcal mol^{-1} and -21.7 kcal mol^{-1} for **4** and **5**, respectively, indicating that one-electron reduction readily occurs.

$$1/2\text{Mn} + (\text{Ph}_3\text{P})_2\text{Ni}^{\text{II}}(\text{Ph})\text{Cl} \rightarrow 1/2\text{MnCl}_2 + (\text{Ph}_3\text{P})_2\text{Ni}^{\text{I}}(\text{Ph}) \qquad (1)$$

The next step is the CO_2 insertion into the Ni(I)–Ph bond of **6**; see Scheme 2. CO_2 approaches **6** to form an η^2-coordinate nickel(I)–carbon dioxide adduct Ni(Ph)(PPh_3)_2(CO_2) **7**; see Fig. 2. One C=O bond of CO_2 which coordinates with the nickel centre becomes somewhat longer to 1.243 Å than that (1.169 Å) of free CO_2, while another C=O bond distance is similar to that of free CO_2. The Ni–C

[a] *Fukui Institute for Fundamental Chemistry, Kyoto University, Nishihiraki-cho, Takano, Sakyo-ku 606-8103, Japan. E-mail: sakaki.shigeyoshi.47e@st.kyoto-u.ac.jp*
[b] *Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan*
† Electronic supplementary information (ESI) available: Computational details, population changes, SCF energies and Cartesian coordinates. See DOI: 10.1039/c3cc45836a
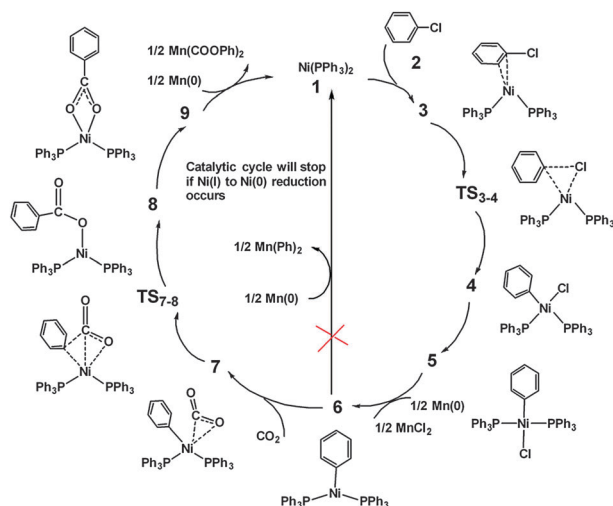
Scheme 2 Full catalytic cycle of Ni(0)-catalyzed carboxylation of phenyl chloride with CO_2.
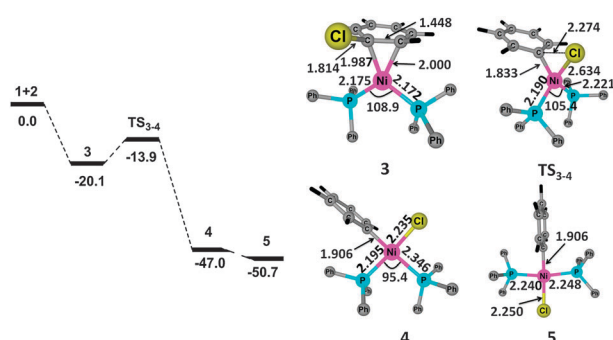

Fig. 2 Optimized geometries involved in the CO_2 insertion into the Ni–Ph bond of **6** and **5** (TS$_{5-10}$). Bond lengths are given in angstroms and angles in degrees. Ph on the phosphine represents the phenyl ring.

Fig. 1 Gibbs energy profile and geometries of important species in the oxidative addition of phenyl chloride to Ni(PPh$_3$)$_2$. All energy values are given in kcal mol^{-1}. Bond lengths are given in angstroms and angles in degrees. Ph on the phosphine represents the phenyl ring.

Fig. 3 Gibbs energy profile for CO_2 insertion reaction. (a) CO_2 insertion into the Ni(I)–Ph bond of **6**. (b) CO_2 insertion into the Ni(II)–Ph bond of **5**. All the values are given in kcal mol^{-1}.

upon one-electron reduction of **8** and **9** are evaluated to be -3.1 and -0.2 kcal mol^{-1}, respectively; see eqn (2).

$$1/2\text{Mn} + (\text{Ph}_3\text{P})_2\text{Ni}^{\text{I}}(\text{O}_2\text{CPh}) \rightarrow 1/2\text{Mn}(\text{O}_2\text{CPh})_2 + \text{Ni}^0(\text{PPh}_3)_2 \quad (2)$$

Thus, it is clearly concluded that phenyl chloride is easily converted to benzoate with CO_2 by the Ni(PPh$_3$)$_2$–Mn system and Ni(I) species plays an important role in the CO_2 insertion step.

To find the reason why one-electron reduction of **4** or **5** is necessary, we investigated the CO_2 insertion into the Ni(II)–Ph bond of **5**; we employed **5** here because **5** is similar to **6**. As shown in Fig. 3b, the CO_2 insertion needs a very large $\Delta G^{0\neq}$ value of 31.7 kcal mol^{-1}, indicating that the CO_2 insertion into the Ni(II)–Ph bond is very difficult. Hence, one-electron reduction of **5** to **6** is indispensable in this catalytic cycle.

The next question is why CO_2 is much more easily inserted into the Ni(I)–Ph bond than into the Ni(II)–Ph bond. In the insertion reaction, the Ni–Ph bond is broken and the Ni–O$_2$CPh bond is formed. The Ni(I)–Ph bond energy (63.3 kcal mol^{-1}) is considerably larger than the Ni(II)–Ph one (54.5 kcal mol^{-1}); see Table S2 (ESI†) for the definition of bond energy. But, the Ni(I)–η^2-O$_2$CPh bond energy (99.7 kcal mol^{-1}) is much larger than the Ni(II)–η^1-OCOPh one (67.7 kcal mol^{-1}). These results clearly indicate that the significantly large exothermicity of the CO_2 insertion into the Ni(I)–Ph bond arises from the formation of a

and Ni–O distances of 1.990 and 2.114 Å in **7** indicate that CO_2 takes an η^2-side-on coordination form. The nickel(0) carbon dioxide complex has a longer C=O distance, shorter Ni–O and Ni–C distances, and a smaller OCO angle than those of **7**, indicating that the Ni–CO_2 interaction is weaker in **7** than in the Ni(0) complex; see Fig. S4 (ESI†) for Ni(PPh$_3$)$_2$(CO_2). Actually, the binding energy of the CO_2 coordination is calculated to be -5.1 kcal mol^{-1} for **7** and -25.6 kcal mol^{-1} for Ni(PPh$_3$)$_2$(CO_2). The electron population of CO_2 increases by 0.434 e in Ni(PPh$_3$)$_2$(CO_2) and 0.295 e in **7**, while the d-orbital population of Ni decreases by 0.287 e in Ni(PPh$_3$)$_2$(CO_2) and 0.151 e in **7**; see Table S1, ESI.† These results strongly indicate that the larger charge transfer (CT) from the Ni centre to CO_2 is responsible for the larger binding energy in Ni(PPh$_3$)$_2$(CO_2) than in **7**, as discussed previously.[19] From **7**, CO_2 is easily inserted into the Ni(I)–Ph bond with a very small $\Delta G^{0\neq}$ value of 1.4 kcal mol^{-1} to afford an η^1-coordinate Ni$^{\text{I}}$(PPh$_3$)$_2$(η^1-OCOPh) **8** through a transition state TS$_{7-8}$, as shown in Fig. 3a. Complex **8** further isomerizes to a more stable η^2-coordinate Ni(I) carboxylate **9**; see Fig. 2 for **8** and **9** and ESI,† page S7, for the isomerization of **8** to **9**.

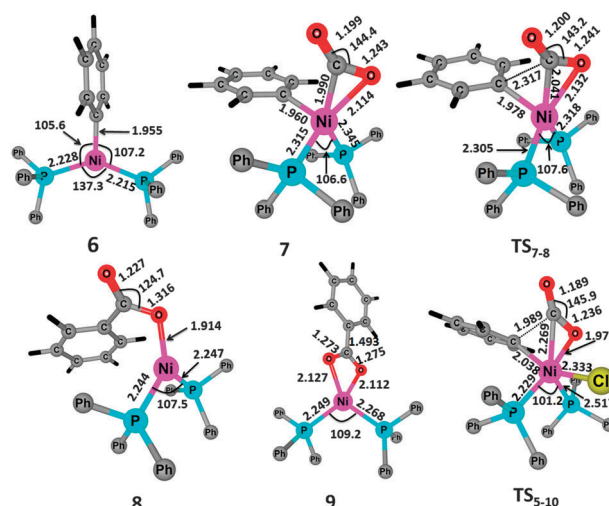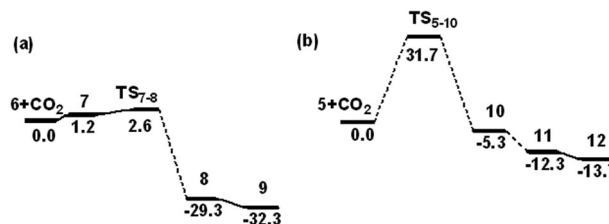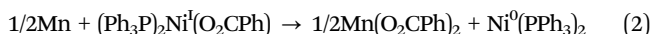To complete the catalytic cycle, **8** or **9** must undergo one-electron reduction by Mn. The Gibbs energy changes (ΔG_2^0)
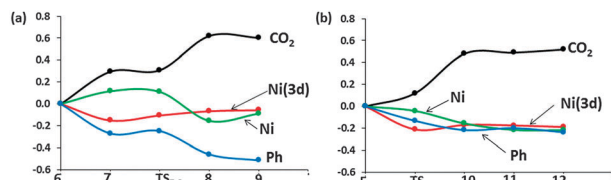
Fig. 4 Population changes in the CO_2 insertion reaction. (a) CO_2 insertion into the Ni(I)–Ph bond of **6**. (b) CO_2 insertion into the Ni(II)–Ph bond of **5**. Positive values represent an increase in population relative to **6** in (a) and relative to **5** in (b).

very strong Ni(I)–η^2-O_2CPh bond. However, it should be noted that the difference in the $\Delta G^{0\neq}$ value (29.1 kcal mol^{-1}) between $\mathbf{TS_{7\text{-}8}}$ and $\mathbf{TS_{5\text{-}10}}$ is much larger than the difference in the ΔG^0 value (18.6 kcal mol^{-1}) between **9** and **12**; see Fig. 3. This means that the interaction of the transition state is more favourable in **6** than in **5**. In both of the CO_2 insertion reactions of **5** and **6**, the electron population of CO_2 significantly increases, while that of the Ph moiety considerably decreases, as shown in Fig. 4. These results indicate that the CT from the Ni–Ph moiety to CO_2 plays an important role in the CO_2 insertion. Based on the population changes, the CO_2 insertion into the Ni–Ph bond is characterized as the nucleophilic attack of phenyl carbon to the carbon of CO_2; see Fig. S9 (ESI†) for MOs participating in the CT. It should be noted that the electron population of CO_2 increases much more and that of the Ph group decreases much more in the CO_2 insertion into the Ni(I)–Ph bond than in the insertion into the Ni(II)–Ph bond, as shown in Fig. 4. These results lead to the conclusion that the CT from the Ph moiety to CO_2 occurs more strongly in **6** than in **5** and the stronger CT in $\mathbf{TS_{7\text{-}8}}$ arises from the more negatively charged Ph group in **6** than in **5**; the NBO charge of Ph is -0.287 e in **5** and -0.547 e in **6**.

One more important question is why **6** does not undergo further one-electron reduction to afford a Ni(0) species but **9** undergoes one-electron reduction to afford a Ni(0) species. To construct this catalytic cycle, one-electron reduction must occur in **4**, **5**, **8** and **9** but not in **6**. As shown in eqn (3), the Gibbs free energy change (ΔG^0_3) for one-electron reduction of **6** is 0.4 kcal mol^{-1}, which is much larger than ΔG^0_1 and moderately larger than ΔG^0_2. These results provide the computational evidence that one-electron reduction of **6** cannot occur unlike that of **9**. In both eqn (2) and (3), Ni(PPh$_3$)$_2$ is formed. The differences are found in another product and in the reactant; Ni(η^2-O_2CPh)(Ph$_3$)$_2$ is a reactant and Mn(O_2CPh)$_2$ is a product in eqn (2) but Ni(Ph)(Ph$_3$)$_2$ is a reactant and MnPh$_2$ is a product in eqn (3). The Mn–Ph bond energy (54.2 kcal mol^{-1}) is much smaller than that (92.5 kcal mol^{-1}) of the Mn–η^2-O_2CPh one and its energy difference is larger than that between the Ni-(η^2-O_2CPh) and Ni–Ph bond energies; see Table S2 (ESI†).

$$1/2\,Mn + (Ph_3P)_2Ni^IPh \rightarrow 1/2\,MnPh_2 + Ni^0(PPh_3)_2 \qquad (3)$$
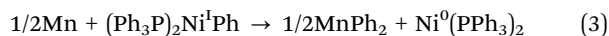
Another factor can be found in the LUMO energies of **6** and **9**; it is calculated to be -0.77 eV and -0.81 eV, respectively. This result suggests that the redox potential is more negative in **6** than in **9**. This is because the Ph group is electron-donating but η^2-O_2CPh is not. Also, the CO_2 coordination with Ni(Ph)(PPh$_3$)$_2$ easily occurs with a small $\Delta G^{\neq}$ value than its one-electron reduction; see above. Thus, **6** cannot undergo one-electron reduction under

these reaction conditions. It is concluded that **5** and **9** easily undergo one-electron reduction but **6** cannot.

In conclusion, we successfully elucidated the reaction mechanism including a Ni(I) intermediate. This is the first report providing the clear evidence indicating that the formation of a Ni(I) intermediate is crucial.

Notes and references

1 D. J. Darensbourg, *Inorg. Chem.*, 2010, **49**, 10765.
2 (*a*) S. N. Riduan and Y. Zhang, *Dalton Trans.*, 2010, **39**, 3347; (*b*) Y. Tsuji and T. Fujihara, *Chem. Commun.*, 2012, **48**, 9956; (*c*) P. Braunstein, D. Matt and D. Nobe, *Chem. Rev.*, 1988, **88**, 747; (*d*) D. H. Gibson, *Chem. Rev.*, 1996, **96**, 2063.
3 (*a*) M. Mikkelsen, M. Jørgensen and F. C. Krebs, *Energy Environ. Sci.*, 2010, **3**, 43; (*b*) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann and F. E. Kühn, *Angew. Chem., Int. Ed.*, 2011, **50**, 8510; (*c*) D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388.
4 L. J. Gooßen, N. Rodríguez and K. Gooßen, *Angew. Chem., Int. Ed.*, 2008, **47**, 3100.
5 (*a*) A. Metzger, S. Bernhardt, G. Manolikakes and P. Knochel, *Angew. Chem., Int. Ed.*, 2010, **49**, 4665; (*b*) H. Ochiai, M. Jang, K. Hirano, H. Yorimitsu and K. Oshima, *Org. Lett.*, 2012, **10**, 2681; (*c*) C. S. Yeung and V. M. Dong, *J. Am. Chem. Soc.*, 2008, **130**, 7826.
6 I. I. F. Boogaerts, G. C. Fortman, M. R. L. Furst, C. S. J. Cazin and S. P. Nolan, *Angew. Chem., Int. Ed.*, 2010, **49**, 8674.
7 (*a*) I. I. F. Boogaerts and S. P. Nolan, *J. Am. Chem. Soc.*, 2010, **132**, 8858; (*b*) H. Mizuno, J. Takaya and N. Iwasawa, *J. Am. Chem. Soc.*, 2011, **133**, 1251; (*c*) A. Uhe, M. Hölscher and W. Leitner, *Chem.–Eur. J.*, 2012, **18**, 170; (*d*) A. Ariafard, F. Zarkoob, H. Batebi, R. Stranger and B. F. Yates, *Organometallics*, 2011, **30**, 6218; (*e*) L. Ackermann, *Angew. Chem., Int. Ed.*, 2013, **50**, 3842; (*f*) W.-J. Yoo, M. G. Capdevila, X. Du and S. Kobayashi, *Org. Lett.*, 2012, **14**, 5326; (*g*) H. Inomata, K. Ogata, S.-I. Fukuzawa and Z. Hou, *Org. Lett.*, 2012, **14**, 3986; (*h*) L. Zhang, J. Cheng, T. Ohishi and Z. Hou, *Angew. Chem., Int. Ed.*, 2010, **49**, 8670.
8 (*a*) C. M. Williams, J. B. Johnson and T. Rovis, *J. Am. Chem. Soc.*, 2008, **130**, 14936; (*b*) M. L. Lejkowski, R. Lindner, T. Kageyama, G. E. Bódizs, P. N. Plessow, I. B. Müller, A. Schäfer, F. Rominger, P. Hofmann, C. Futter, S. A. Schunk and M. Limbach, *Chem.–Eur. J.*, 2012, **18**, 14017.
9 Y. Dingyia and Z. Yugen, *Green Chem.*, 2011, **13**, 1275.
10 A. W. Kleij, *ChemCatChem*, 2013, **5**, 113.
11 A. Correa and R. Martin, *J. Am. Chem. Soc.*, 2009, **131**, 15974.
12 T. Fujihara, K. Nogi, T. Xu, J. Terao and Y. Tsuji, *J. Am. Chem. Soc.*, 2012, **134**, 9106.
13 T. León, A. Correa and R. Martin, *J. Am. Chem. Soc.*, 2013, **135**, 1221.
14 (*a*) S. L. Zultanski and G. C. Fu, *J. Am. Chem. Soc.*, 2013, **135**, 624; (*b*) P. N. Plessow, L. Weigel, R. Lindner, A. Schäfer, F. Rominger, M. Limbach and P. Hofmann, *Organometallics*, 2013, **32**, 3327.
15 S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787.
16 (*a*) Full description of computational details is provided in ESI†; (*b*) M. J. Frisch, *et al.*, *Gaussian 09, Revision B.01*, Gaussian, Inc., Wallingford, CT, 2010, Complete reference is provided in the ESI†.
17 In Scheme 1, the (PPh$_3$)$_2$Ni^{II}Cl$_2$ catalyst is used as a starting material. It can be reduced to (PPh$_3$)$_2$Ni^0 in the presence of Mn; Mn + (PPh$_3$)$_2$Ni^{II}Cl$_2$ → MnCl$_2$ + (PPh$_3$)$_2$Ni^0. The ΔG^0 for this process is evaluated to be -43.9 kcal mol^{-1}, indicating that the formation of Ni(0) species occurs readily.
18 (*a*) We employed Mn atom as a simple model of the Mn powder. But, comparison of ΔG^0 among eqn (1)–(3) is reasonably made here, because the error caused by the use of one Mn is cancelled in the comparison. The free energy of redox reaction (ΔG^0) is used as a measure of the ease of electron transfer; (*b*) Z. Li, S. L. Zhang, Y. Fu, Q. X. Guo and L. Liu, *J. Am. Chem. Soc.*, 2009, **131**, 8815; (*c*) NEt$_4$I is considered to assist the electron transfer from Mn metal to a nickel complex.
19 S. Sakaki, K. Kitaura and K. Morokuma, *Inorg. Chem.*, 1982, **21**, 760.