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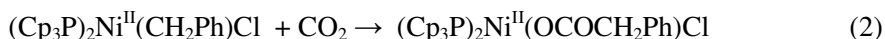
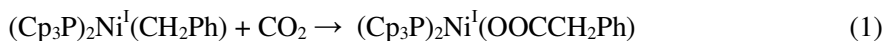
CO₂ Insertion into Ni(I)-Alkyl and Ni(II)-Alkyl Bonds. Interesting Differences

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[Introduction] The conversion of carbon dioxide (CO₂) to useful chemicals is one of the most escalating areas of research. Aryl halide is one of the best substrates for the synthesis of carboxylic acid from CO₂. However, a direct CO₂ insertion into aryl halide bond is not easy. In this context, the recently reported Ni-catalyzed direct carboxylation of PhCH₂Cl with CO₂ is considered efficient CO₂ transformation reaction, where Ni(PCp₃)₂ (Cp = cyclopentyl) is employed as a catalyst. Experimental results suggest that the Ni(I) species participates in the CO₂ insertion, as shown in Eq. (1), but the evidence has not been provided.

We theoretically investigated this reaction to unravel the reason why Ni(I) species is crucial for this reaction and why Ni(II) is not suitable for the CO₂ insertion; see Eq. (2).



[Computational Details] All geometries were optimized with the dispersion corrected B3LYP-D functional with BS-I basis set system. In BS-I, Lan12Tz(f) basis set for Ni, 6-31G(d) for H, C, O, P, and 6-31+G(d) for Cl were employed. The solvent effect of *N,N*-dimethylformamide (DMF) was estimated by conductor-like polarizable continuum model (CPCM). A better basis system (BS-II) was used for evaluation of solvent effect. In BS-II, we employed Lan12Tz(f) basis set for Ni, cc-pVDZ for H, C, O, P, and aug-cc-pVDZ for Cl. The reliability of the B3LYP-D functional is verified here with the oxidative addition to a model complex Ni(PH₃)₂; Ni(PH₃)₂ + PhCH₂Cl → Ni(PhCH₂)(Cl)(PH₃)₂. The calculated activation energy agrees well with that of CCSD(T).

[Results and Discussion] Geometry and energy changes for the CO₂ insertion into the Ni(I)-CH₂Ph bond of (Cp₃P)₂Ni^I(CH₂Ph) are shown in Figure 1. First, CO₂ coordinates to the Ni(I) centre to form η²-coordinated CO₂ complex **2**, from which CO₂ insertion occurs to afford a carboxylate complex **3** through a four-member transition state **TS**_{2,3} with an activation barrier of 6.6 kcal/mol. Complex **3** isomerises to the most stable η²-coordinated carboxylate complex (Cp₃P)₂Ni^I(η²-O₂CCH₂Ph) **4**.

The CO₂ insertion into the Ni(II)-CH₂Ph of (Cp₃P)₂Ni^{II}(CH₂Ph)Cl **5** occurs through a four-member transition state without the formation of a Ni(II)-CO₂ complex, as shown in Figure 2. The activation barrier is 38.8 kcal/mol, which is substantially larger than that into the Ni(I)-CH₂Ph bond. These results indicate that the Ni(II)-CH₂Ph is not reactive for CO₂ insertion but the Ni(I)-CH₂Ph is reactive.

We investigated the reasons from the bond energy and the interaction in the transition state. By the CO₂ insertion reaction, the Ni-C bond is broken and the Ni-OCOR bond (R=CH₂Ph)

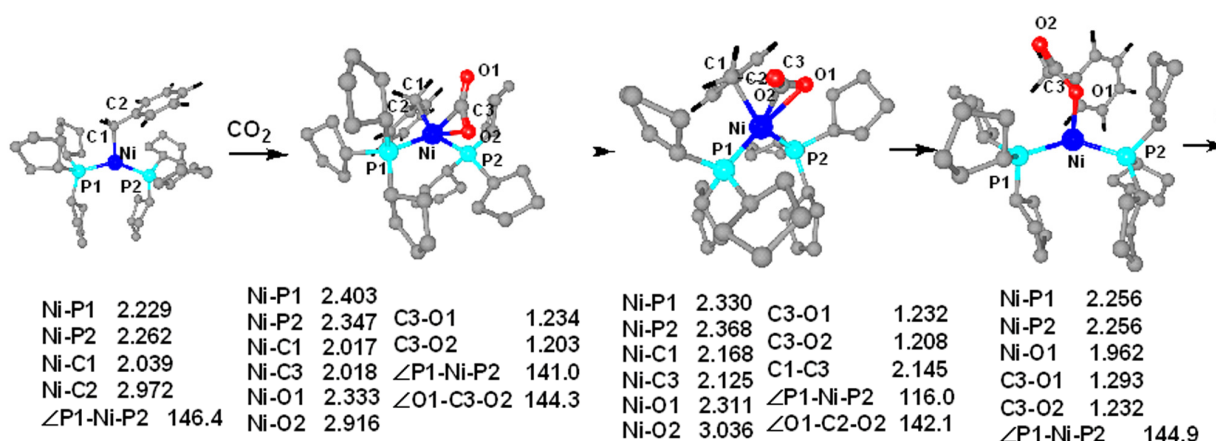


Figure 1. Geometry and energy changes in the CO₂ insertion of Ni(I)-CH₂Ph bond of (Cp₃P)₂Ni^I(CH₂Ph). Gibbs free energies are provided in parenthesis. All the bond lengths are in angstroms and angles are in degrees.

is formed. The Ni(I)-CH₂Ph bond is calculated to be stronger (42.5 kcal/mol) than the Ni(II)-CH₂Ph bond (32.1 kcal/mol) but the Ni(I)-OCOR bond (103.3 kcal/mol) is much stronger than the Ni(II)-OCOR bond (79.7 kcal/mol). NBO population analysis of TS_{2,3} and TS_{5,6} suggest that charge transfer (CT) from the Ni(I)-benzyl moiety to CO₂ much more strongly occurs than that from the Ni(II)-benzyl. This is because the benzyl group is more negatively charged in the Ni(I)-benzyl complex than in the Ni(II)-benzyl group.

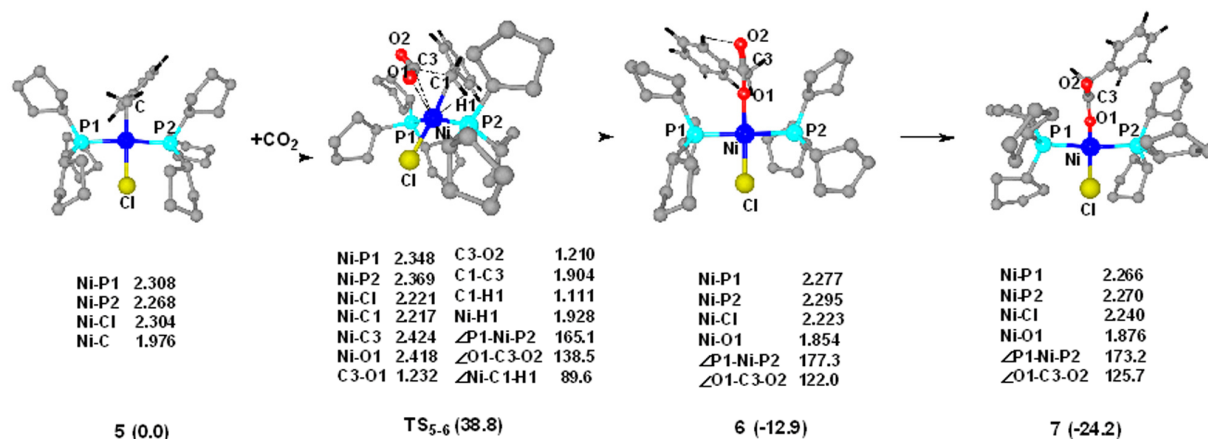


Figure 2. Geometry and energy changes in the CO₂ insertion of Ni(II)-CH₂Ph bond of (Cp₃P)₂Ni^{II}(CH₂Ph)(Cl). Gibbs free energies are provided in parenthesis. All the bond lengths are in angstroms and angles are in degrees.

Thus, it is concluded that the CO₂ insertion into Ni(I)-alkyl bond is thermodynamically and kinetically favourable.