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Cobalt−Carbene Complex with Single-Bond Character: Intermediate for the Cobalt Complex-Catalyzed Cyclopropanation

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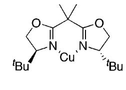
Since the catalytic enantioselective cyclopropanation of olefins with diazoacetates was reported in 1966,[1] a wide variety of transition-metal complex catalysts have been developed.[2] For example, the Cu(I)−bis(oxazoline) complex[3] and the Ru(II)−2,6-di(2-oxazolin-2-yl)pyridine (pybox) complex[4] are some of the most efficient catalysts, and the 3-oxobutylideneaminato−Co complex[5] and the salen−Co complex[6] have been developed by our group and Katsuki's. However, the reaction mechanism and the nature of the metal−carbene intermediates have been rarely studied until recently.[7,8] Therefore, the combination of experimental and theoretical studies on the metal−carbene intermediates for cyclopropanation would provide a promising and reliable methodology for design of novel complexes of effective catalysis. It is generally considered that metal−carbene carbon bonds in carbene complexes should be double-bonded; however, in this communication, we report that the Co−carbene carbon bond of the 3-oxobutylideneaminato− and the salen−Co−carbene complex shows a strong single-bonded character.

The most probable mechanism of the transition-metal-complex-catalyzed cyclopropanation is considered as follows: a transition-metal complex reacts with diazoacetates to generate the metal−carbene intermediate, and then the intermediate reacts with alkenes to afford cyclopropane.

To investigate the nature of the intermediate, the Cu−bis(oxazoline) complex **1** and the Ru−pybox complex **2** were adopted as references, and the 3-oxobutylideneaminato−Co(II) **3** and −Co(III) **4** complexes, and the salen−Co(II) **5** and Co(III)−**6** complexes were representatives of the Co complexes. The reaction of these complexes with methyl diazoacetate was traced by time-resolved FT-IR spectroscopy[9] focused on the stretching of the C═O double bond of the ester group. The absorption wavenumbers are shown in Table 1. The band for the stretching of the C═O of the methyl diazoacetate was observed at 1699 cm^{-1}. A weak band assigned to the stretching of the C═O of the Cu− and the Ru−carbene complex appeared at 1650 and 1651 cm^{-1}, respectively.[10] However, those of the Co−carbene complexes were significantly shifted ca. 50 cm^{-1} downward. A typical spectrum for the reaction of the Co complex **3** and methyl diazoacetate is shown in Figure 1. A new peak at 1595 cm^{-1} was clearly observed, which is assigned to the stretching of the C═O of the Co−carbene complex. The generation of the Co−carbene complexes from complexes **4**−**6** could be confirmed by the FAB-mass spectroscopy. Therefore, these experiments indicated that the double bond of the carbonyl group of the Co−carbene complexes was significantly weaker than that of the Cu− or Ru−carbene complex.

Table 1. Absorption Wavenumber of the Carbonyl Groups of the Generated Metal−Carbene Complexes (cm^{-1})



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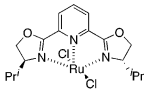

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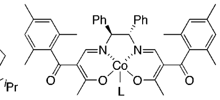
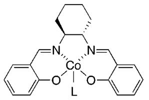


3 L = *N*-methylimidazole
4 L = Cl



5 L = *N*-methylimidazole
6 L = I

complex	N_2CHCO_2Me	**1**	**2**	**3**	**4**	**5**	**6**
$\nu_{C=O}$	1699	1650	1651	1595	1600	1601	1617

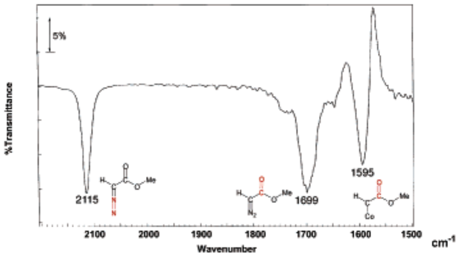


Figure 1. Time-resolved IR-spectrum of the reaction of the cobalt(II) complex **3** and methyl diazoacetate (after 2 min).

For a comprehensive account of this extraordinary downward-shift of the C═O stretching of the Co−carbene complexes, a theoretical analysis[11] of the model complexes **7**−**12** was performed using the B3LYP[12] method with LANL2DZ,[13] 3-21G*, and 6-31G* as basis sets (the 3-21G* basis set was substituted for 6-31G* in the case of the ruthenium atom.) The Cu complex **7** and the Ru complex **8** were analyzed in the singlet states based on the theoretical[7] and experimental[8] studies previously reported. The doublet and quartet states were calculated for the Co(II) complexes **9** and **11**, and it was found that the doublet states were more stable.[14] The triplet and quintet states were calculated for the Co(III) complexes **10** and **12**, and the triplet states were more stable.[15] A conformational analysis of the ester moiety of complexes **9**−**12** resulted in three stable conformers as energy minima for each spin multiplicity.[16] Although the conformer with the ester group located between two nitrogen atoms of the ligand was the most stable in all the spin states, attaching the sterically demanding substituent on the ethylene-bridge should destabilize these conformers. Hence, the conformer with the ester group located between the nitrogen and oxygen atoms was, hereafter, adopted for the wavenumber analysis.

The wavenumber of the C═O stretching for the most stable multiplicity is summarized in Table 2. Since a scaling factor for the correction of the calculated frequencies is not provided, a correlation between experimental and calculated results was depicted (Figure 2). A correlation coefficient greater than 0.88 was obtained in each basis set.[17] Therefore, it is reasonable to consider that the theoretical analysis is in full accord with the observation that the C═O stretching of the Co−carbene complexes shifted downward.

For further elucidation of these phenomena, the bond orders were calculated by the natural bond orbital analysis[18] of the metal−carbene carbon bond and the carbon−oxygen bond of the C═O (Table 3). It should be pointed out here that the bond orders of the Cu−carbene carbon and the Ru−carbene carbon are about 1.7,

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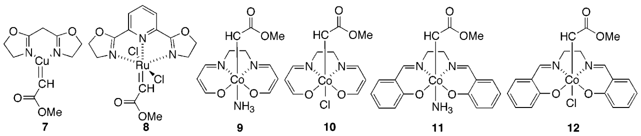
Table 2. Vibrational Frequencies of the Carbonyl Group (cm^{-1})



$\nu_{C=O}$	N_2CHCO_2Me	7	8	9	10	11	12
LANL2DZ	1668	1588	1629	1521	1523	1522	1523
3-21G*	1749	1615	1677	1581	1579	1588	1581
6-31G*	1804	1744	1770	1681	1688	1676	1688

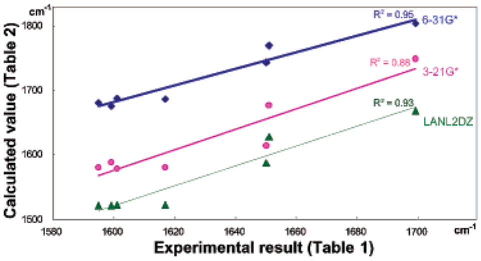
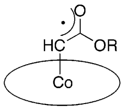


Figure 2. Correlation diagram between the experimental and calculated results.

Table 3. Bond Orderes and Bond Distances of the Metal−Carbene Carbon and Carbonyl Group (B3LYP/6-31G*)

	bond order		bond distance (Å)	
complex	M−Cc	C═O	M−Cc	C═O
7	1.706	1.812	1.781	1.223
8	1.684	1.847	1.867	1.219
9	0.868	1.391	1.886	1.231
10	0.781	1.410	1.918	1.228
11	0.861	1.417	1.887	1.230
12	0.793	1.415	1.913	1.230

while, those of the Co−carbene carbon range from 0.78 to 0.87. The bond orders of the C═O of the Co−carbene complexes **9**−**12** are obviously smaller than that of the carbene complexes **7** and **8**. Furthermore, the Co−C bond was longer than the Cu−C or Ru−C bond, and C═O double bond in the Co complexes **9**−**12** was longer than that in the Cu complex **7** and the Ru complex **8**. These results indicated that the Cu−C bond or Ru−C bond is characterized as a double bond, whereas the Co−C bond should be characterized as an extraordinary single bond.[19] This single-bond character is explained as follows: As for the Co(II) complex, the electronic structure of the d orbital of the Co atom at the ground state is described as $(d_{x^2-y^2})^2$ $(d_{yz})^2$ $(d_{xz})^2$ $(d_{z^2})^1$. During the reaction of the Co atom with diazoacetate, an orbital interaction between the d_{z^2} of the Co and the p_z orbital of the diazoacetate occurs, and after the release of nitrogen, one σ-bond and one surplus electron on the carbene carbon was generated.[20] This electron cannot be used for the formation of the π-bond, since an energetically unfavorable one-electron excitation from the fully occupied d_{xz} or d_{yz} orbital of the Co atom to the d_{xy} orbital should be required. Hence, the surplus electron was delocalized between the carbene carbon and adjacent carbonyl group depicted as **13**, and as a result, a downward-shift in the C═O stretching wavenumber was observed. As for the Co(III) complex, an explanation similar to the Co(II) complex was possible.



13

In summary, it is generally considered that metal−carbene carbon bonds in carbene complexes for cyclopropanation should be double-bonded; however, the theoretical and FT-IR analyses revealed that the Co−C bond of the 3-oxobutylideneaminato or the salen−Co−carbene complexes was characterized as a single bond.

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Supporting Information Available: FT-IR spectra, ^{13}C NMR, energies, and structures obtained from the conformational analysis of the Co complexes **9**−**12** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) IR spectra were measured in the ATR configuration using a liquid cell under N_2. A background scan was first done with a solution of 0.1 mmol complex in 2 mL of dichloromethane. After 0.1 mmol methyl diazoacetate was added to the circle cell as time zero, the sample measurements of the reaction media were performed.
(10) When the complex **1** or **2** was used, a peak corresponding to the dimeric products, dimethyl fumalate and dimethyl maleate, appeared around 1731 cm^{-1} immediately after the addition of the methyl diazoacetate. On the contrary, when the Co complexes **3**−**6** were used, the dimers were hardly detected.
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(14) The measurement of magnetic susceptibility of Co complex revealed that the spin multiplicity of the starting Co(II) and Co(III) complex was doublet and triplet, respectively.
(15) Valid structures of the Co(III) complexes **10** and **12** could not be obtained in the singlet states.
(16) Relative energies are shown in the Supporting Information.
(17) The influence of the basis set is described in the Supporting Information.
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(20) Since p-orbital of carbene carbon conjugated with C═O bond, s-*cis* conformation was the most stable.

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