FT-IR and Theoretical Analysis of the Characteristic Bonding Properties in the Multiplet Metal Porphyrin Carbene Complexes

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FT-IR and theoretical studies of the d^6 and d^7-porphyrin carbene complexes revealed that the metal–$C_{carbene}$ bond is a double bond in the singlet state, while the metal–$C_{carbene}$ bond is a single bond in the multiplet state. Since the radical on the $C_{carbene}$ delocalized to the α-carbonyl group, the stretching of the C=O double bond shifted downward in the multiplet states.

Various carbene complexes, such as the Fischer-type carbene complexes,[1] Grubbs' catalysts,[2] and cyclopropanation-catalysts,[3] have been utilized for organic syntheses, although almost all of them are diamagnetic and the properties of the paramagnetic carbene complexes have been scarcely studied. Recently, we reported the extraordinary single bond character of the carbene carbon–metal bond of the salen- and ketoiminato cobalt carbene complexes.[4] In this communication, we would like to describe the detailed investigation of porphyrin carbene complexes to generalize the nature of the bonding character in relation to the spin states of the porphyrin complexes.

The metal–porphyrin complexes **1**–**4** with various spin states were examined in order to elucidate the nature of the paramagnetic metal porphyrin carbene complexes (Figure 1). Fe(TPP) **1** is in the triplet state and Co(TPP) **2** is in the doublet state,[5] whereas Co(TPP)Cl **3** and Ru(TMP)CO **4** are in the singlet states. It was reported that these porphyrin complexes reacted with diazo compounds to generate metal-carbene species.[6] The density functional calculations were performed for the model complexes **5**–**8** to evaluate the energies of each spin state.[7] B3LYP[8] was used with LANL2DZ[9] and 6-31G* (3-21G* for ruthenium) as the basis sets. These calculations revealed that the triplet was the most stable for Fe(Por) **5** and the doublet was more stable than the quartet for Co(Por) **6**,[10] in accord with a previous report,[11] and that the singlet was the most stable for Co(Por)Cl **7** and Ru(Por)CO **8**.

The reaction of the porphyrin complexes with ethyl diazoacetate was traced by time-resolved FT-IR spectroscopy focused on the C=O stretching in the ester group.[12] The C=O stretching of ethyl diazoacetate was observed at 1692–1694 cm^{-1}. For Fe(TPP) **1** and Co(TPP) **2**, the bands at 1594 and 1597 cm^{-1} appeared and could be assigned to the C=O stretching of their carbene complexes. On the other hand, a weak band appeared at 1646 cm^{-1} for Co(TPP)Cl **3** and Ru(TMP)CO **4**, which could be assigned to that of the Ru and Co carbene complexes. The band of 1742 cm^{-1} for the C=O stretching of the diethyl fumarate and diethyl maleate remarkably increased in the Co complex **3**[13] or the Ru complex **4** catalyzed reaction. These results indicated that the dimerization of ethyl diazoacetate crucially depended on the nature of the centered metal of the complexes.

The observed frequencies for the C=O stretching of the porphyrin carbene complexes were categorized into two classes, around 1600 and 1646 cm^{-1} (Table 1). The former frequencies (1594–1597 cm^{-1}) were observed for the metal porphyrin complexes in the multiplet states, while the latter category (1646 cm^{-1}) was observed in the singlet states. For the singlet Co(TPP)Cl, the C=O stretching was assigned as 1646 cm^{-1} whereas that of the triplet ketoiminato Co(III)Cl was at 1600 cm^{-1}.[4] It is worth mentioning again that the centered metal of the porphyrin complexes was not essential but their spin states were crucial for these categorization.

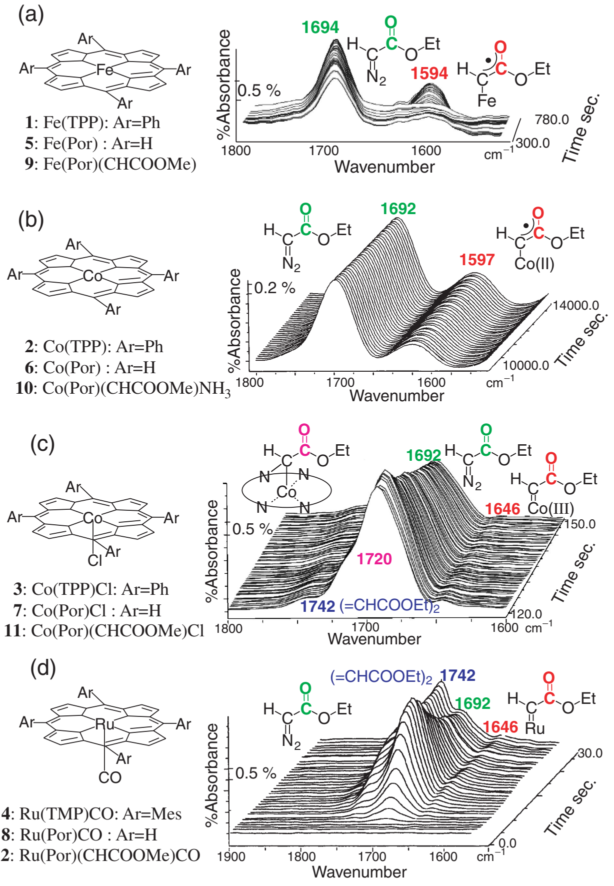

Figure 1. Time-resolved IR spectrum of the reaction of (a) Fe(TPP) **1** and N_2CHCO_2Et (b) Co(TPP) **2** and N_2CHCO_2Et (c) Co(TPP)Cl **3** and N_2CHCO_2Et (d) Ru(TMP)CO **4** and N_2CHCO_2Et.

The density functional calculations of the carbene complexes **9**–**12** were performed for the model of the corresponding porphyrin complexes experimentally observed to estimate their frequencies.[14,15] Two rotational isomers concerning the ester moiety for each carbene complex were obtained after conformational analysis and the more stable conformer was employed to evaluate the correlation between the experimental and calculated frequencies. A correlation coefficient greater than 0.90 was obtained in both basis sets.[16] Therefore, the theoretical analysis was consistent with the observation that the C=O stretching of the paramagnetic metal porphyrin carbene complexes shifted downward about 50 $\mathrm{cm^{-1}}$ relative to that of the diamagnetic metal porphyrin carbene complexes.

The bond order of the metal–$\mathrm{C_{carbene}}$ bond was estimated by the natural bond orbital analysis (Table 1).[17] The Co–$\mathrm{C_{carbene}}$ bond of $\mathrm{Co^{III}}$(Por)Cl carbene complex **11** in the singlet state was calculated to be a double bond. On the contrary, the $\mathrm{Co^{II}}$(Por) carbene complex **10** was in a doublet state and its Co–$\mathrm{C_{carbene}}$ bond was a single bond. It could be deduced that the multiplet porphyrin carbene complexes have single metal–$\mathrm{C_{carbene}}$ bonds while the singlet porphyrin carbene complexes have double bonds. Consistent with this bonding character, the bond length of the cobalt–carbene carbon of **10** was longer than that of **11** by 0.093 Å. When considering of the bond order (ca. 1.4) of C=O in the multiplet carbene complexes, a radical on the carbene carbon was delocalized over the α-carbonyl group similar to the ketoiminato cobalt complexes.[4] The most stable conformer for each spin state also suggested the delocalization; e.g., the carbonyl plane is perpendicular to the π-plane of the metal–$\mathrm{C_{carbene}}$ bond in the singlet complexes. Thus, no conjugation could be expected between them. On the contrary, the radical could be effectively delocalized because the carbonyl plane was located parallel to the π-plane of the metal–$\mathrm{C_{carbene}}$ bond in the multiplet carbene complexes. Therefore, the bond distances of the C=O of the paramagnetic carbene complexes (**9** and **10** : 1.227 Å) were longer than those of the diamagnetic carbene complexes (**11** and **12** : 1.216 Å), and the bond order of the C=O of the paramagnetic complexes was smaller by 0.4 than that of the diamagnetic complexes.

Table 1. Observed and calculated wavenumbers of C=O stretching, bond order and length of porphyrin carbene complexes

Complex Exp./Calcd.		Fe(TPP) **1/9**	Co(TPP) **2/10**	Co(TPP)Cl **3/11**	Ru(TMP)CO **4/12**
Multiplicity		Triplet	Doublet	Singlet	Singlet
$\nu_{\mathrm{C=O}}$ (Exp.)	$/\mathrm{cm^{-1}}$	1594	1597	1646	1646
$\nu_{\mathrm{C=O}}$ (LANL2DZ)	$/\mathrm{cm^{-1}}$	1560	1563	1607	1638
$\nu_{\mathrm{C=O}}$ (6-31G*)	$/\mathrm{cm^{-1}}$	1699	1697	1770	1782
Bond Order (M–Cc)		0.89	0.87	1.37	1.71
Bond Order (C=O)		1.42	1.42	1.83	1.85
Bond Length (M–Cc)	/Å	1.858	1.884	1.791	1.859
Bond Length (C=O)	/Å	1.227	1.227	1.216	1.216

In summary, the $\mathrm{d^6}$ and $\mathrm{d^7}$-porphyrin carbene complexes were investigated by time-resolved FT-IR and DFT analyses and it was observed that the generated carbene from these complexes have the same spin state as the starting porphyrin complexes. In the singlet states, the metal–$\mathrm{C_{carbene}}$ bond is a double bond, although in the multiplet states, the metal–$\mathrm{C_{carbene}}$ bond is a single bond. The radical on the $\mathrm{C_{carbene}}$ delocalizes over the α-carbonyl group, and as a result, the C=O stretching shifted downward. The present observation is the first characterization of the paramagnetic porphyrin carbene complexes[6h] and also suggested that the spin states of the catalyst would affect the character of the carbene intermediates. It is expected that the control of the spin states of the complexes could be significant for the design of the catalyst.

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10 As a model for the addition of *N*-methylimidazole, the calculation of $\mathrm{Co(Por)NH_3}$ was also examined. It was found that the doublet was more stable than the quartet for $\mathrm{Co(Por)NH_3}$, similar to Co(Por).

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13 The band at 1720 $\mathrm{cm^{-1}}$ for the stretching of the C=O of the migrated complex smoothly increased. See Ref. 6i.

14 All the spin states of the carbene complexes **9**–**12** were calculated. For the Co(II) carbene complex **10**, the doublet was more stable than the quartet states. The singlet was the most stable for the Co(III)–Cl and Ru(II) carbene complexes, **11** and **12**. Though the triplet was slightly less stable than the singlet for the model Fe(II) carbene complex **9**, phenyl groups might stabilize the triplet states deduced from the observed frequency.

15 According to Ref. 6d, it was proposed that the carbon monooxide of Ru(TMP)CO was released during the reaction with diazoacetate. Therefore, the calculation of Ru(Por)(CHCOOMe) was also performed and results similar to the Ru carbene complex **12** were obtained. The singlet was the most stable ($S^2 = 0$) and the calculated frequencies were 1615 $\mathrm{cm^{-1}}$ at UB3LYP/LANL2DZ and 1778 $\mathrm{cm^{-1}}$ at UB3LYP/6-31G* for Ru(Por)(CHCOOMe).

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