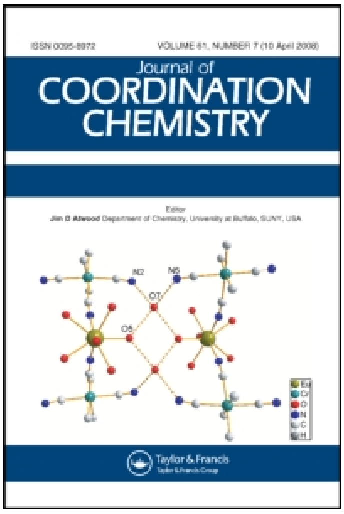

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Paeng, Insook R. and Nakamoto, Kazuo(1991) 'Resonance Raman and Infrared Spectra of Carbene Complexes of Iron Porphyrins Dongsheng Lu', Journal of Coordination Chemistry, 23: 1, 3 — 12
To link to this Article: DOI: 10.1080/00958979109408237
URL: http://dx.doi.org/10.1080/00958979109408237

J. Coord. Chem. 1991, Vol. 23, pp. 3–12
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RESONANCE RAMAN AND INFRARED SPECTRA OF CARBENE COMPLEXES OF IRON PORPHYRINS

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(Received June 12, 1990)

The resonance Raman and infrared spectra of four carbene complexes, Fe(TTP)CCl_2, Fe(TPP)$^{13}CCl_2$, Fe(TPP)CBr_2 and Fe(TMP)CCl_2 were measured in the solid state. Based on normal coordinate calculations and observed isotopic shifts by CCl_2/$^{13}CCl_2$ substitution, the ν(Fe=C), $\nu_a(CCl_2)$ and $\nu_s(CCl_2)$ vibrations were assigned at 1274, 878 and 437 cm^{-1}, respectively. The bromo analogue exhibits these bands at 1270, 823 and 364 cm^{-1}, respectively. All TPP complexes exhibit the spin-state sensitive band (ν_2) at 1569 cm^{-1} and the oxidation-state sensitive band (ν_4) at 1370 cm^{-1}, thus suggesting that the Fe atoms in these carbene complexes are low-spin Fe(IV).

Keyword: Carbene complexes of iron porphyrins

INTRODUCTION

Previously, we obtained oxo-iron(IV) porphyrins(ferrylporphyrins) *via* laser photolysis of dioxygen adducts of iron(II) porphyrins in O_2 matrices at ~15 K, and located their ν(Fe=O) vibrations near 850 cm^{-1}.[1,2]

$$\mathrm{Fe(por)O_2} \xrightarrow{h\nu} \mathrm{O{=}Fe(por)} + 1/2\ \mathrm{O_2}$$

Recently, we prepared nitridoiron(V) porphyrins *via* laser photolysis of azidoiron(III) porphyrins at ~30 K, and observed their ν(Fe≡N) vibrations near 876 cm^{-1}.[3,4]

$$\mathrm{Fe(por)N_3} \xrightarrow{h\nu} \mathrm{N{\equiv}Fe(por)} + \mathrm{N_2}$$

These high-valent iron porphyrins are stable only at low temperatures, and coverted to μ-oxo and μ-nitrido dimers, respectively, when warmed to higher temperatures. A logical extension of these investigations would be the preparation and characterization of carbidoiron porphyrins *via* laser photolysis of iron porphyrins containing axially carbon-bonded ligands. For example, carbene complexes of iron porphyrins may serve as a precursor for this reaction:

$$\mathrm{Fe(por)CX_2} \xrightarrow{h\nu} \mathrm{:C{=}Fe(por)?} + \mathrm{X_2}(\mathrm{X\text{: a halogen}})\,.$$

It is of great interest to find out whether such carbido complexes can be formed *via* laser photolysis and if so what electronic structures the iron and carbon atoms adopt in these complexes.

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Carbene complexes of iron porphyrins were first prepared by Mansuy *et al.*[5] in 1977. Thus far, X-ray analysis[6] and Mössbauer measurements[7] have been carried out on Fe(TPP)CCl_2 (TPP: tetraphenylporphyrinato anion). As far as vibrational spectroscopy is concerned, Chottard *et al.*[8] measured resonance Raman (RR) spectra of a number of Fe(TPP)(L)(L′) complexes including several carbene complexes. Based on vibrational frequencies of several structure-sensitive bands, these workers assigned the carbene complexes as low-spin Fe(II) species. On the other hand, Mössbauer studies[7] suggested Fe(TPP)CCl_2 to contain low-spin Fe(IV). In this paper, we report the RR and IR spectra of Fe(TPP)CCl_2, Fe(TPP)$^{13}CCl_2$, Fe(TPP)CBr_2 and Fe(TMP)CCl_2 (TMP: tetramesitylporphyrinato anion), and have assigned TPP vibrations as well as the Fe=CX_2 group vibrations. Normal coordinate calculations were carried out on the Fe=CX_2 fragment.

EXPERIMENTAL

Compounds

Fe(por)Cl (por: TPP or TMP), (100 mg, *ca* 1.4×10^{-4} mol) was dissolved in 50 cm^3 of CH_2Cl_2–MeOH (9/1 by volume) under an argon atmosphere, and stirred in the presence of excess iron powder (300 mg). After a few min, degassed CCl_4 ($^{13}CCl_4$) or solid CBr_4 was added, and the solution stirred vigorously for 2 hr at ~20°C. Formation of Fe(TPP)(CX_2) in solution can be confirmed by electronic spectroscopy (λ_{max}, 409, 525 and 550 nm (shoulder), Fig. 1).[9] After filtration, the solution was washed with deionized water, dried over Na_2SO_4 and evaporated. The solid residue thus obtained was dissolved in and recrystallized from 25 cm^3 CH_2Cl_2–MeOH (1/9 by volume). The sample was kept under vacuum (10^{-2}–10^{-3} mm Hg) for 10 hr. The dried carbene complex was obtained as purple-red crystals. All the compounds exhibit the electronic spectra shown in Figure 1. In addition, the CCl_2 complexes exhibit the C–Cl stretching bands at 872 cm^{-1} in their IR spectra.[5] None of these compounds exhibits the IR band characteristic of the μ-carbido dimer, ν_a(FeCFe) at 940 cm^{-1}.[10] Although carbene complexes are stable for a long time if kept as solids under vacuum, their benzene solutions show signs of decomposition after one hour as the band at 525 nm becomes hypsochromic and hypochromic (see Fig. 1).

Spectral Measurements

Thin films of the carbene complexes were prepared by evaporating their benzene solutions on the surface of a cold tip which was then cooled down below 25 K by a CTI 20/70 cryocooler. RR spectra of thin films were recorded on a Spex 1403 double monochromator equipped with a Hamamatsu R-928 photomultiplier and a Spex DM1B controller. Excitations were made by using a Coherent I-100-K3 Kr ion laser (406.7 nm). The laser power at the sample was *ca* 3 mW. In order to avoid sample decomposition by the laser beam, a backscattering geometry was set up using a small mirror and a cylindrical lens to create a line focus on the sample surface. Since the line image on the surface was *ca* 4 mm long, it was possible to expose the sample to at least 20-fold lower light density than with conventional point focusing. The accuracy of frequency reading was ±1 cm^{-1}.

The electronic absorption spectra (benzene solution) were measured on a Hewlett-

Packard 8452A diode array spectrophotometer. The accuracy of wavelength reading was ±1 nm. The IR spectra (KBr pellets) were measured on a Beckman 4260 infrared spectrophotometer. The accuracy of frequency reading was $\pm 1.5\,\text{cm}^{-1}$.

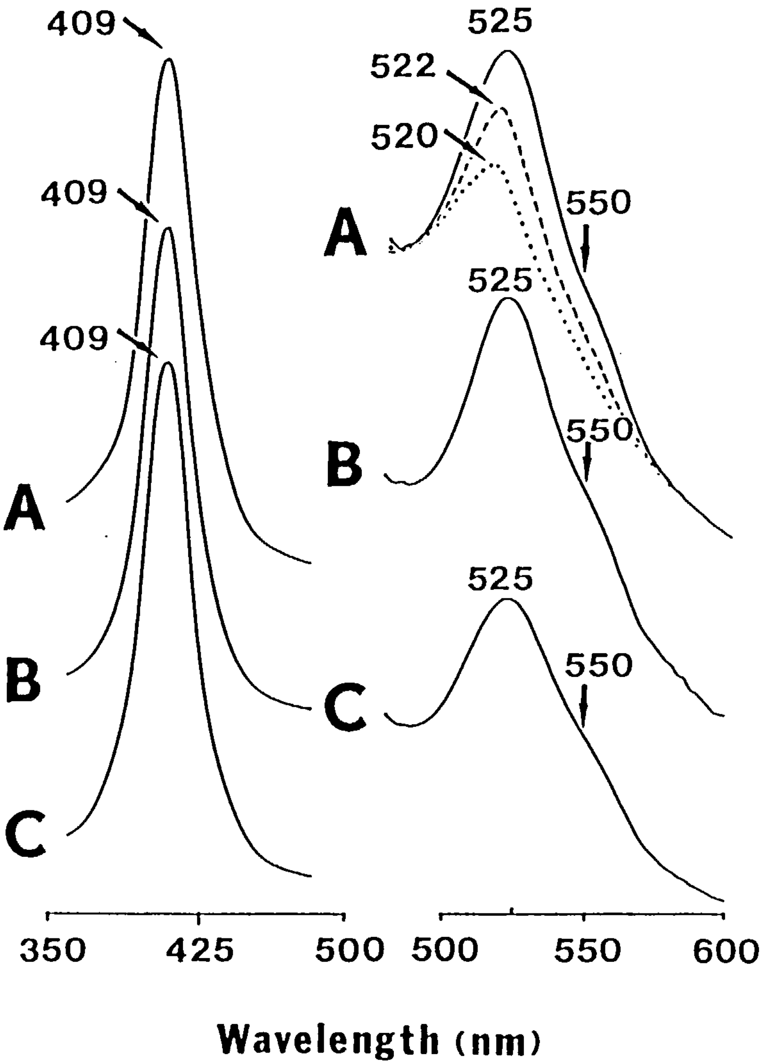


FIGURE 1 Electronic spectra of Fe(TPP)CCl_2 (trace A), Fe(TPP)$^{13}CCl_2$ (trace B) and Fe(TPP)CBr_2 (trace C) in benzene solution. The broken and dotted lines indicate the spectra obtained after 60 and 90 min., respectively.

RESULTS AND DISCUSSION

Before discussing the RR spectra of thin films at ~25 K, it is important to note that carbene complexes are easily decomposed by high power laser beams. Figure 2

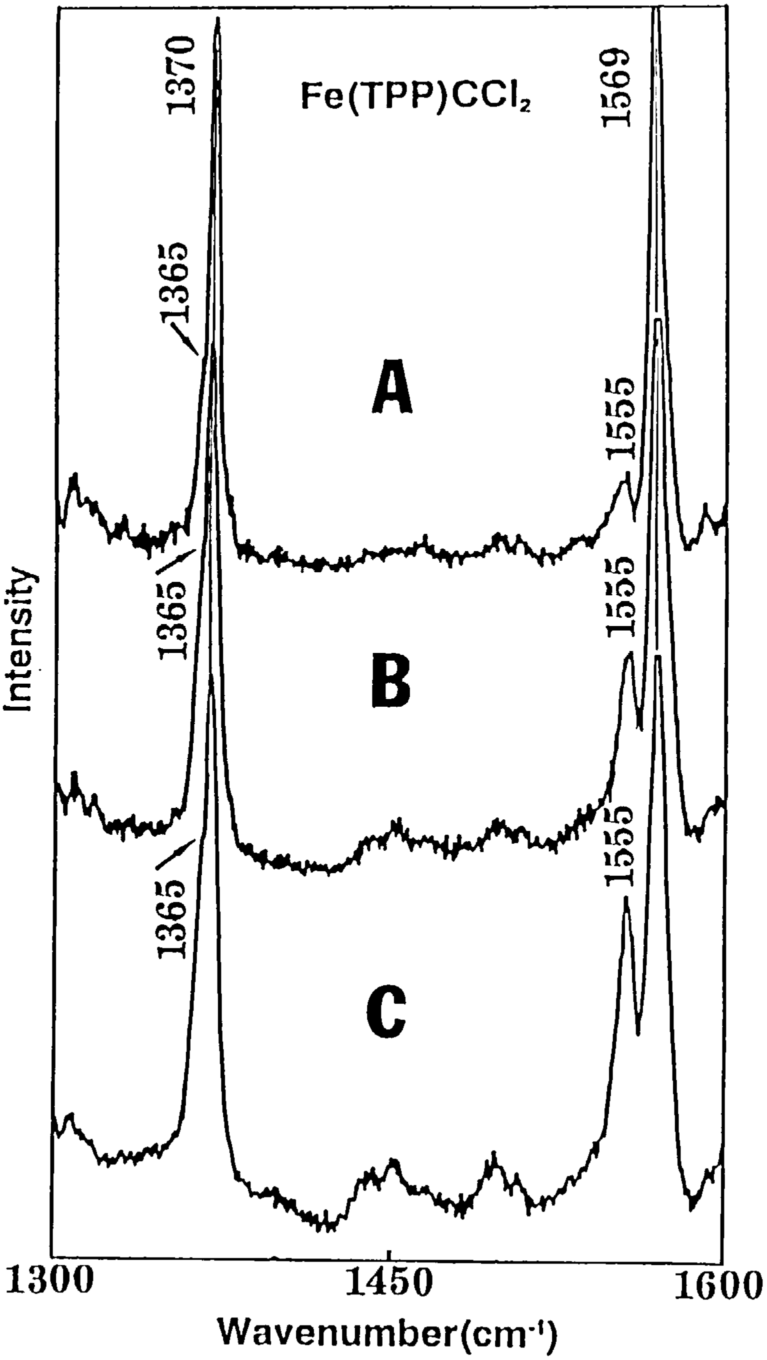
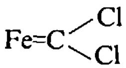
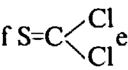


FIGURE 2 RR spectra of Fe(TPP)CCl$_2$ in the 1600–1300 cm^{-1} region; traces A, B and C were obtained with laser power of 3, 10 and 50 mW, respectively (film state, ~25 K, 406.7 nm excitation).

compares the RR spectra of Fe(TPP)CCl_2 in the high frequency region obtained by using 3 (trace A), 10 (trace B) and 50 mW (trace C) laser power. To minimize photodecomposition, all the RR spectra reported in this investigation were obtained by combining the spectra of four regions (1800–1400, 1400–1000, 1000–600 and 600–200 cm^{-1}), which were recorded separately. For each region, a fresh sample spot was placed in the laser focus for each scan and 7–8 scans were made within a period of 20-25 minutes. As seen in trace A, the RR spectrum of Fe(TPP)CCl_2 exhibits Band A (oxidation state marker) at 1370 cm^{-1} and Band D (spin state marker) at 1569 cm^{-1}.[2] These frequencies are similar to those of several Fe(TPP)L-type complexes which are known to contain low spin Fe(IV).[2] We therefore conclude that the Fe atoms in the carbene complexes are also low spin Fe(IV). When the laser power is increased, new bands grow at 1365 and 1555 cm^{-1}, which are close to those in Fe(TPP)Cl (Fe(III), high spin).[2] These results suggest that Fe(TPP)CCl_2 is decomposed to Fe(TPP)Cl by laser irradiation under these conditions.

Traces, A, B and C of Figure 3 show the RR spectra (406.7 nm excitation, 3 mW) of Fe(TPP)CCl_2, Fe(TPP)$^{13}CCl_2$ and Fe(TPP)CBr_2 (thin films at ~25 K). The bands at 1274, 878 and 437 cm^{-1} in trace A are shifted to 1247, 850 and 435 cm^{-1}, respectively, by CCl_2/$^{13}CCl_2$ substitution. Thus, these vibrations must involve the motion of the carbon atom. As shown later, they are assigned to the ν(Fe=C), $\nu_a(CCl_2)$, and $\nu_s(CCl_2)$, respectively, by normal coordinate calculations. By CCl_2/CBr_2 substitution, the ν(Fe=C) shifts only slightly (to 1270 cm^{-1}) while the $\nu_a(CCl_2)$ and $\nu_s(CCl_2)$ shift markedly; 878 to 823 and 437 to 364 cm^{-1}, respectively (trace C). Figure 4 shows the IR spectra (KBr pellet) of Fe(TPP)CCl_2 (trace A), Fe(TPP)$^{13}CCl_2$ (trace B) and Fe(TPP)CBr_2 (trace C). The $\nu_a(CCl_2)$ band at 872 cm^{-1} is shifted to *ca* 840 cm^{-1} by CCl_2/$^{13}CCl_2$ substitution, and to 815 cm^{-1} by CCl_2/CBr_2 substitution. These IR frequencies are close to those obtained in the RR spectra of thin films at ~25 K. Their strong appearance in IR spectra suggests that these bands are due to the antisymmetric CCl_2 group vibrations. Further support comes from Raman polarization measurements of Fe(TPP)CCl_2 in benzene solution which indicated that the 878 cm^{-1} band is depolarized ($\rho \sim 0.8$) while the 437 cm^{-1} band is polarized ($\rho \sim 0.4$).

Normal Coordinate Analysis

In order to assign axial ligand vibrations, normal coordinate analysis was carried out on a planar  $Fe{=}C\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$ model of C_{2v} symmetry. The bond distances (Fe–C, 1.83 Å and C–Cl, 1.75 Å)[6] and bond angles ($<$ClCCl = 112 and FeCCl = 124°)[11] were taken from the literature. Table I lists the internal coordinates and force constants (general valence force field) used. The latter are very close to that of  $S{=}C\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$ except for the Fe=C stretching force constant.[12] Table II compares the observed and calculated frequencies for Fe(TPP)CCl_2 and its ^{13}C analogue. The agreement is satisfactory although two bending modes near 250 cm^{-1} were not observed. In Table III, we compare the vibrational frequencies of the Fe=CX_2 fragment with those of S=CCl_2[12] and S=CBr_2.[13]

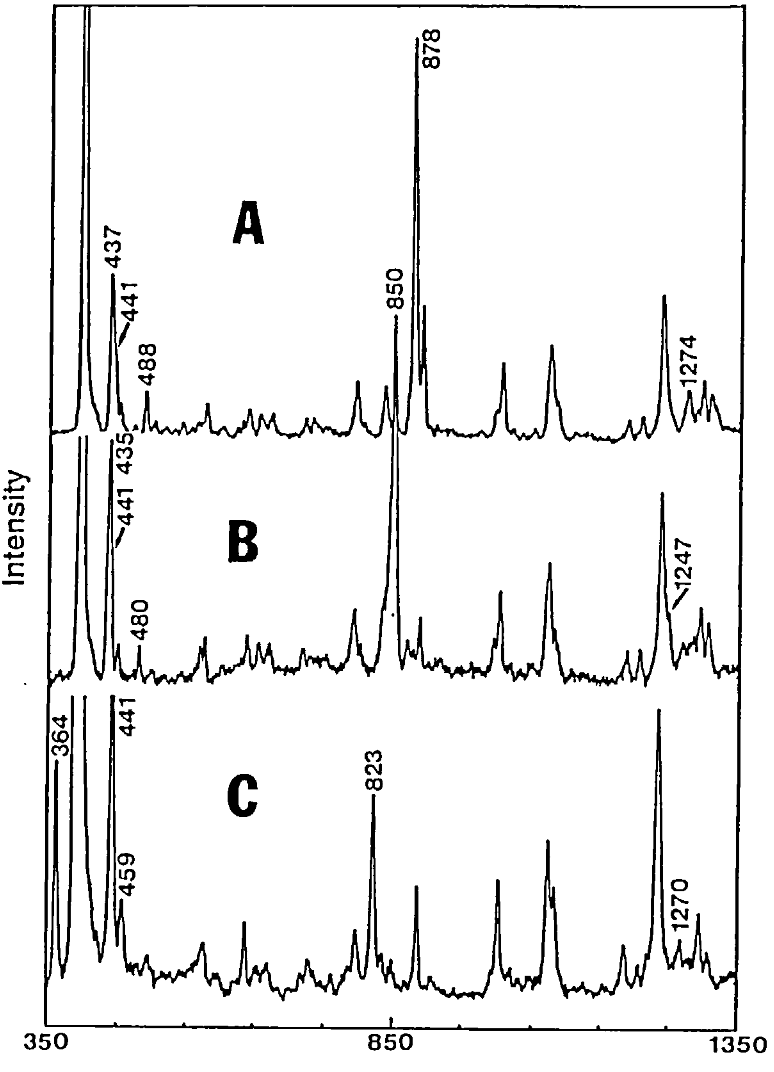


FIGURE 3 RR spectra of Fe(TPP)CCl_2 (trace A), Fe(TPP)$^{13}CCl_2$ (trace B) and Fe(TPP)CBr_2 (trace C) in the 1350–350 cm^{-1} region (film state, ~25 K, 406.7 nm excitation).

It was of our particular interest to locate the ν(Fe=C) vibration in the RR spectra since no such assignments had been made previously. As seen in Figure 3, we noted a rather weak band at 1274 cm^{-1} for Fe(TPP)CCl_2 which shifts to 1247 cm^{-1} by CCl_2/$^{13}CCl_2$ substitution. This frequency is slightly higher than the ν(S=C) of S=CCl_2 (1135 cm^{-1}).[12] Using a Fe=C stretching force constant (7.6 mdyn/Å) which is slightly larger than the S=C stretching force constant of S=CCl_2 (6.24 mdyn/Å),[12] we were able to obtain perfect agreement between the observed and calculated frequencies (1274 cm^{-1}).

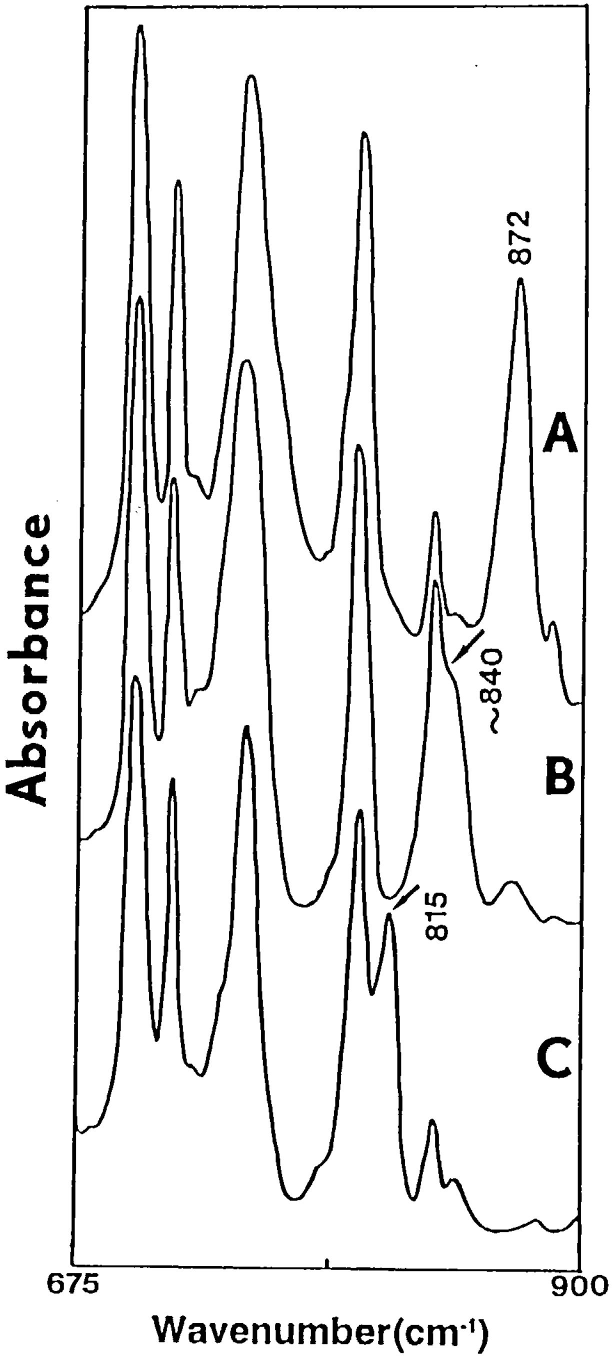


FIGURE 4 IR spectra of Fe(TPP)CCl$_2$ (trace A), Fe(TPP)^{13}CCl$_2$ (trace B) and Fe(TPP)CBr$_2$ (trace C) in KBr pellets.

TABLE I
Internal coordinates and force constants (mdyn/Å).

f_1 = K(Fe=C)	7.6	f_5 = K (out of plane)	0.63
f_2 = K(C-Cl)	2.78	f_6 = k(Rr)	0.29
f_3 = H(ClCCl)	1.30	f_7 = k(Rβ)	0.50
f_4 = H(FeCCl)	0.90	f_8 = k(rα)	0.24
		f_9 = k(rβ)	0.60

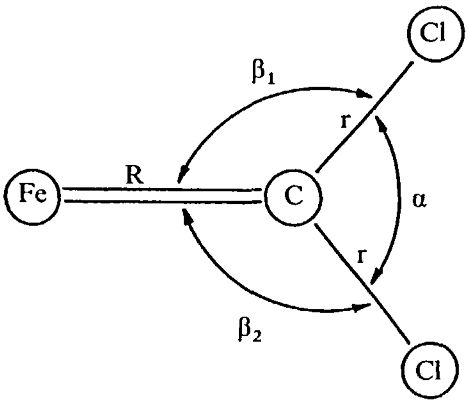


TABLE II
Comparison of observed and calculated frequencies (cm^{-1}).

		^{12}C		^{13}C		
		Obs.	Calc.	Obs.	Calc.	Assignment
A_1	ν_1	1274	1275	1247	1230	ν(Fe=C) (77%) + $\nu_s(CCl_2)$ (16%)
	ν_2	437	439	435	439	$\nu_s(CCl_2)$ (50%) + ν(Fe=C) (24%)
	ν_3		252		251	δ(ClCCl) (66%) + $\nu_s(CCl_2)$ (29%)
B_1	ν_4	878	878	850	848	$\nu_a(CCl_2)$ (86%) + δ(FeCCl) (23%)
	ν_5		231		230	δ(FeCCl) (77%) + $\nu_a(CCl_2)$ (26%)
B_2	ν_6	488	489	480	471	Out-of-plane

TABLE III
Vibrational frequencies (cm^{-1}) of $S=CX_2$ and $Fe=CX_2$ (X=Cl and Br).

	$X=YZ_2$	$S=CCl_2$[a]	$S=CBr_2$[b]	Fe(TPP)CCl_2	Fe(TMP)CCl_2	Fe(TPP)CBr_2
ν_1	ν(X=Y)	1135(1103[b])	1116(1082)	1274(1247)	1278(1240)	1270
ν_2	$\nu_s(YZ_2)$	500	367	437(435)	438(437)	364
ν_3	δ(ZYZ)	295	181			
ν_4	$\nu_a(YZ_2)$	813	697	878(850)	883(849)	823
ν_5	δ(XYZ)	305	230			
ν_6	Out-of-plane	471	415	488(480)	450(443)	459

[a] Ref. 12. [b] Ref. 13; numbers in parentheses indicate frequencies of ^{13}C derivatives.

Table IV lists the observed frequencies and band assignments for all the bands in the 1600–200 cm^{-1} region. Assignments of TPP vibrations are based on recent normal coordinate calculations by Li *et al.*[14]

In this work, we have shown that the RR spectra of unstable carbene complexes of iron porphyrins can be obtained if proper precautions are taken during the measurements. We have made complete band assignments on the Fe=CCl_2 fragment by combining the CCl_2/$^{13}CCl_2$ isotope shift data with normal coordinate calculations. In agreement with previous Mössbauer studies, we found that the Fe atom in Fe(TPP)CCl_2 is low-spin Fe(IV). Although the ultimate goal of our investigation was to obtain novel carbidoiron porphyrins *via* laser photolysis, it was not possible to detect the formation of such species during the decomposition process. Further studies are needed to determine whether such carbido complexes can be formed and detected if different experimental conditions are employed.

TABLE IV
Observed frequencies (cm^{-1}) and band assignments.

	Fe(TPP)CCl_2	Fe(TPP)CBr_2	Assignment[a]
ν_2	1569	1569	$\nu(C_\alpha C_m) + \nu(C_\beta C_\beta) + \nu(CC)_{Ph}$
ν_4	1370	1370	$\nu(C_\alpha C_\beta) + \nu(NC_\alpha) + \delta(C_\alpha NC_\alpha) + \delta(C_\alpha C_m)$
	1274	1270	$\nu(Fe{=}C) + \nu_s(CCl_2)/\nu_s(CBr_2)$[b]
ν_1	1237	1237	$\delta(C_m{-}Ph) + \nu(NC_\alpha) + \nu(CC)_{Ph} + \delta(CCH_{Ph})$
ν_9	1074	1075	$\delta(C_\beta H) + \nu(C_\beta C_\beta)$
ν_6	1005	1005	$\nu(C_\alpha C_\beta) + \nu(NC_\alpha) + \nu(CC)_{Ph}$
ν_7	890	888	$\delta(CC)_{Ph} + \nu(CC)_{Ph} + \nu(C_\alpha C_\beta)$
	878	823	$\nu_a(CCl_2)/\nu_a(CBr_2) + \delta(FeCCl)/\delta(FeCBr)$[b]
	488	459	Out-of-plane ($FeCX_2$)[b]
ν_{33}	441(Sh)	441	$\delta(C_\alpha C_m) + \nu(C_\alpha C_m) + \nu(C_\alpha C_\beta)$
	437	364	$\nu_s(CCl_2)/\nu_s(CBr_2) + \nu(Fe{=}C)$[b]
ν_8	396	394	$\nu(FeN) + \delta(C_\alpha C_m C_\alpha) + \nu(C_\alpha C_m)$
	203	203	$\nu(C_\alpha C_{Ph}) + \nu(C_\alpha C_m) + \delta(CC)$

[a] Ref. 14. [b] This work.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (DMB-8613741). The authors thank Mr. Songzhou Hu of Marquette University for his assistance with the normal coordinate calculations.

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