corresponding band of compound I and its model compound has never been observed so far partly due to photolability of the sample. Recently we succeeded in observing the $\nu_{Fe=O}$ Raman band of the ferryl porphyrin π cation radical for the first time by using the spinning cell at $-80\ ^\circ C$ and the OMA detection system. Here we discuss the nature of the $Fe^{IV}=O$ bond of the ferryl porphyrin π cation radical.

The so called green complex,[5a] which was characterized as the oxo–iron(IV) porphyrin π cation radical,[13] was derived in the Raman or absorption cell by the reaction of (5,10,15,20-tetramesitylporphyrinato)iron(III) chloride [(TMP)Fe^{III}Cl] with *m*-chloroperoxybenzoic acid (*m*-CPBA) in a CH_2Cl_2/CH_3OH (5:1 in volume) mixed solvent at $-80\ ^\circ C$ according to Groves et al.[5a] The [18]O labeled *m*-CPBA was synthesized from *m*-chlorobenzoyl chloride and $H_2{}^{18}O_2$ in the presence of NaOH.[23] Raman scattering was excited at 406.7 nm with the power as low as possible (5 mW) and detected with a diode array detector (PAR 1420) attached to a Spex 1404 double monochromator. The sample was spun (1800 rpm) at $-80\ ^\circ C$, and the measurements were finished within a few minutes after exposure of the sample to the laser beam.

Figure 1 shows the visible absorption spectra of (TMP)Fe^{III}Cl and the green complex observed at $-80\ ^\circ C$. These are in reasonable agreement with the reported spectra.[5a] Figure 2 shows the resonance Raman spectra of the green complex. Spectra (A) and (C) were observed for the green complexes obtained from the [16]O- and [18]O-*m*-CPBA, respectively. Only the 828-cm^{-1} band in spectrum (A) was a new band upon the formation of the green complex and this band was shifted to 792 cm^{-1} with [18]O as shown in spectrum (C). For an isolated $\nu_{Fe=O}$ vibration, the $\nu(^{18}O)/\nu(^{16}O)$ frequency ratio is calculated to be 0.956, and accordingly the expected isotopic frequency shift ($\Delta\nu$) is $0.044\nu_{Fe=O}(^{16}O)$. If we assume $\nu_{Fe=O}(^{16}O) = 828$ cm^{-1}, the expected shift would be $\Delta\nu = 36.4$ cm^{-1}, which agrees remarkably well with the observed shift. When the green complex was derived from (TMP)^{54}Fe^{III}Cl and [16]O-*m*-CPBA, spectrum (E) was obtained. The 4-cm^{-1} shift of the 828-cm^{-1} band to a higher frequency is coincident with the expected isotopic frequency shift (3.4 cm^{-1}). Consequently, the 828-cm^{-1} band is assigned to the $\nu_{Fe=O}$ band of the green complex. The good agreement between the observed and calculated isotopic frequency shifts means that this mode is scarcely coupled with other porphyrin vibrations.

When the spinning of the cell was stopped without raising temperature, spectra (B) and (D) were obtained for the [16]O- and ^{18}O-derivatives, respectively. The $\nu_{Fe=O}$ bands disappeared and a new band appeared at 843–844 cm^{-1} for both derivatives. This band was present in the spectrum of the ferric compound and exhibited a frequency shift of -4 cm^{-1} upon ^{15}N substitution of four pyrrole nitrogens.[22b] Therefore, the 844-cm^{-1} band cannot be assigned to the $Fe^{IV}=O$ stretching mode of the neutral ferryl complex. At the same time as the spectral change around the 800–850-cm^{-1} region, the spectrum in the higher frequency region above 1200 cm^{-1} changed drastically, and the resultant spectrum resembled that of the ferric complex, suggesting the occurrence of photoreduction by two oxidative units. The one-electron reduced species could not be identified in the present experiment.

Previously we pointed out that the oxo oxygen atom of compound II is exchanged with oxygen atoms of bulk water only when the oxo oxygen atom is hydrogen bonded to the distal histidine.[17b,d] In the original report of the green complex,[5a] on the other hand, incorporation of the [18]O atom into olefin upon addition of $H_2{}^{18}O$ to the green complex was noted. Hence we measured the Raman

spectrum of the [16]O derived green complex in the presence of $H_2{}^{18}O$, but the $\nu_{Fe=O}$ band remained unshifted. Therefore, the oxo oxygen atom in the green complex was not easily exchanged with bulk water under the present conditions.

The $\nu_{Fe=O}$ frequency of (TMP)Fe$^{IV}=O$ in toluene was 843 cm^{-1},[22a] but this frequency is reported to change with surroundings. Out of the reported $\nu_{Fe=O}$ frequencies of the ferryl complexes, that in the oxygen matrix at 15 K is highest (852 cm^{-1}),[19] and the frequency decreases in coordinating solvents: 829 cm^{-1} in THF[20] and 807–820 cm^{-1} in *N*-methylimidazole.[20,21] The coordination number of the green complex has not been clarified yet. The NMR study[24] suggested the presence of weak interactions between the iron ion(IV) and methanol. However, the $\nu_{Fe=O}$ Raman band was identified at the same frequency for the green complex derived in the absence of methanol and also upon addition of acetic acid to it. Judging from this insensitivity of the $\nu_{Fe=O}$ frequency and also from the absence of the EXAFS peak corresponding to the Fe-trans ligand pair,[13] it seems more likely that the green complex which gives rise to the $\nu_{Fe=O}$ Raman band adopts the five coordinate structure. Then, the present observation implies that the oxidation of the porphyrin ring to the cation radical results in slight reduction of the double bond character of the axial $Fe^{IV}=O$ bond.

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Insertion of Carbon Monoxide into Transition-Metal–Acyl Bonds To Form α-Ketoacyl Complexes

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Migratory insertion of CO into transition-metal–*alkyl* bonds to form acyl ligands is one of the most studied of all transition-metal organometallic reactions.[1] In contrast, the insertion of a second CO into a metal–*acyl* bond to form an α-ketoacyl ligand has never been observed, even though a number of the important "double carbonylation" reactions[2–4] could involve such a transformation. However, the only mechanistically studied "double carbonylation" catalyst has been shown to form α-ketoamide

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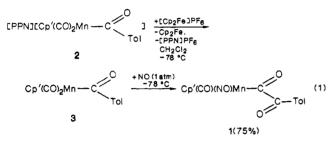(2) (a) Sen, A.; Chen, J.-T.; Vetter, W. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 148. (b) Chen, J.; Sen, A. *J. Am. Chem. Soc.* **1984**, *106*, 1506.

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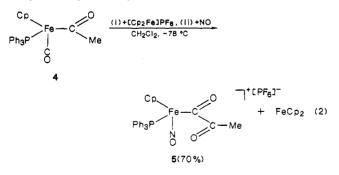8098 *J. Am. Chem. Soc., Vol. 109, No. 26, 1987*

Communications to the Editor

products not by CO insertion into a metal–acyl bond but by reductive-coupling of two acyl ligands.[2,3] Indeed, all previous studies have led to the general conclusion that insertion of CO into a metal–acyl bond is not a likely reaction.[2,3,5] We have now discovered methodology that allows this chemistry to be accomplished by a novel oxidation/NO addition reaction sequence. Reported herein are the first examples of the formal insertion of CO into metal–acyl bonds to form α-ketoacyl ligands.

These reactions were discovered while investigating the mechanism of the earlier described transformation of a carbyne ligand into an α-ketoacyl ligand by addition of NO_2^- to [Cp'-$(CO)_2Mn\equiv CTol]^+$ (Cp' = C_5H_4Me).[6] We have since found that the crystallographically characterized[6] α-ketoacyl product of this reaction, Cp'(CO)(NO)Mn–C{O}C{O}Tol, **1**, can be made directly from the acyl complex [PPN][Cp'(CO)$_2$Mn–C{O}Tol], **2**,[7] by the sequence of reactions shown in eq 1. Cyclic voltammetry (22

2

3

1(75%)

°C, CH_2Cl_2, [Bu_4N]PF$_6$, 100 mV/s) showed that the acyl complex **2** undergoes reversible oxidation at –1.03 mV vs the Cp$_2$Fe/[Cp$_2$Fe]$^+$ couple. The oxidation product Cp'(CO)$_2$Mn–C{O}Tol, **3**, can be chemically prepared by treatment of CH_2Cl_2 solutions of **2** at –78 °C with either of the one-electron oxidants [NO]BF$_4$ or [Cp$_2$Fe]PF$_6$. It shows two ν(CO) bands at 1997 and 1913 cm^{-1} which are $\sim$120 cm^{-1} higher in energy than the 1878 and 1797 cm^{-1} bands of **2**, consistent with an oxidized species. IR monitoring showed that complex **3** survives warmup to room temperature, although it slowly decomposes to CpMn(CO)$_3$ and other unidentified products over a several hour period at 22 °C. Treatment of –78 °C solutions of **2** with bubbling NO gas led immediately to formation of the known α-ketoacyl complex **1**.[6] This species was isolated in 75% recrystallized yield, although IR monitoring showed the reaction to be quantitative. Use of [NO]BF$_4$ as the oxidant of **2** initially gave a $\sim$1:2 mixture of **1** and **3** over a 20-min period at –78 °C, with the former presumably deriving from the NO formed in the oxidation process.

This reaction is not confined to manganese nor to anionic acyl complexes since the neutral iron–acyl Cp(CO)(PPh$_3$)Fe–C{O}Me **4**[8] undergoes a similar transformation to give the new α-ketoacyl complex **5**,[9] eq 2. Complex **5** was isolated as a red-brown solid.

4

5(70%)

It shows a strong ν(NO) band at 1848 cm^{-1} and bands at 1740 (w), 1719 (w), and 1674 (m) cm^{-1} assigned to the α-ketoacyl ligand. α-Ketoacyl complexes such as **5** typically show *four* IR bands in the acyl region due to the presence of s-cis and s-trans rotomers,[3c,6] and the broad three band pattern of **5** is apparently due to overlap of two of these. Particularly diagnostic of the α-ketoacyl ligand of **5** are the two ^{13}C NMR resonances at δ 246.8 (J_{cp} = 17 Hz) and 189.2 (J_{cp} = 4 Hz), respectively, assigned to the α- and β-carbonyl carbons of this ligand. These values compare well to the corresponding α-ketoacyl ligand resonances of Cp'(NO)(PPh$_3$)Mn–C{O}C{O}Tol at δ 292.3 (J_{cp} = 25 Hz) and 189.6 (J_{cp} = 5.5 Hz).[10] Oxidation of acyl complex **4** at –78 °C with [Cp$_2$Fe]PF$_6$ gave disappearance of the IR bands of **4** and the growth of bands at 2008 and 1703 cm^{-1}, respectively, assigned to the carbonyl and acyl ligands of the radical cation [Cp-(CO)(PPh$_3$)Fe–C{O}Me][PF$_6$] (**6**).[11] These bands disappear as those of the product **5** form upon purging the solution with NO gas. Magnuson and Giering[11] have previously shown that acyl complex **4** undergoes quasi-reversible one-electron oxidation to form **6** with $E_{1/2}$ = 0.36 V.

Carbon monoxide insertion into metal–alkyl bonds is well-known to be dramatically accelerated by oxidation of the starting alkyl,[12] but this phenomenon is poorly understood and has never before been seen for acyl complexes as described herein. Only the oxidative promotion of CO insertion into the metal–methyl bond of Cp(CO)(L)Fe–Me has been studied in detail.[11a,13] This reaction was recently shown by Trogler[13] to proceed by an *associative* mechanism involving addition of pyridine to the 17e$^-$ complex [Cp(CO)(PPh$_3$)Fe–Me]$^+$ to form 19e$^-$ [Cp(CO)(PPh$_3$)(py)Fe–Me]$^+$ which then undergoes the migratory-insertion step. We suggest that reactions 1 and 2 proceed by similar addition of NO to the 17e$^-$ radicals **3** and **6** to give *18e$^-$ complexes with the NO ligand binding as a bent 1e$^-$ donor.*[14] However, the nitrosyl ligand strongly prefers a 3e$^-$ linear coordination mode in low-valent organometallic complexes,[15] and this it can achieve either by expelling a CO ligand or inducing insertion of CO into the metal–acyl bond. The latter must be favored in the reactions reported here. Energetically, the transformation of the nitrosyl ligand from a 1e$^-$ to a 3e$^-$ donor provides the driving force for the acyl to α-ketoacyl transformation. The ability of NO to trap and stabilize the intermediates is essential in the carbonyl–acyl coupling, since reaction of solutions of **3** with CO, CH$_3$CN, or PPh$_3$ gave only substituted Cp'Mn(CO)$_2$L complexes.

This work has demonstrated that insertion of CO into metal–acyl bonds is a viable organometallic reaction, although so far it has only been induced by the oxidation/NO addition reaction sequence used herein. We are currently testing the further generality of this methodology for acyl complexes as well as its potential for inducing other difficult insertions.

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