Halide complexes corresponding to hydride **2** may be prepared by treatment of **2** with haloform at low temperature or by reaction of $Cp^*(L)RhI_2$ with 1 equiv of cyclopropyllithium. Conversion of the iodide **4** to the corresponding $\pi$-allyl complex **5** may be achieved[7] by treatment with silver fluoroborate in THF. This salt was isolated in 92% yield as yellow crystals by recrystallization from THF at -40 °C; both $^1H$ and $^{13}C$ NMR data[5] are consistent with its formulation as an $\eta^3$-allyl structure. Treatment of this material with $NaBH_4$ or $LiEt_3BH$ converted it quantitatively (NMR) to metallacycle **3**. This product was isolated from the latter reaction in 90% yield as yellow crystals by slow recrystallization from pentane; it was completely identical in all spectral characteristics with the sample of **3** obtained from the rearrangement of hydrido cyclopropyl complex **2**. Interestingly, treatment with $LiEt_3BD$ led to metallacycle in which the deuterium atom was selectively syn to the cyclopentadienyl ring.[8] Thus the reaction is both regiospecific and completely stereoselective. This result confirms the recent suggestion of Curtis and Eisenstein that $[(C_5H_5)(L)M(\text{allyl})]^+$ systems might provide a second example of this type of reactivity.[3b,9]

Our observations on the generation and chemistry of hydrido cyclopropyl complex **2** require that the kinetic product of reaction of "Cp*RhL" with cyclopropane is formed by insertion into the strong C–H bonds of the organic molecule, whereas the thermodynamic product is formed by insertion into the relatively much weaker C–C bonds. The simplest mechanism that can account for the conversion of **2** to **3** in cyclopropane solvent (cf. Scheme II) suggests that reversible cyclopropane reductive elimination ($k_1$)/C–H activation ($k_{CH}$) takes place above 0 °C. Occasionally, however, C–C insertion ($k_{CC}$) occurs, leading irreversibly to the much more stable metallacycle **3**. This mechanism predicts that replacing the cyclopropane solvent with benzene, known to react with Cp*RhL with a rate constant $k_B$ twice as large as that of $k_{CH}$ for cyclopropane,[2] should divert the rearrangement entirely to hydrido phenyl complex **6**. Accordingly, we generated hydride **2** in cyclopropane, replaced this solvent at low temperature with benzene,[10] and allowed the system to warm to 0 °C. To our surprise, fully 50% of the hydride had still been converted to metallacycle, the remainder giving cyclopropane and hydrido phenyl complex **6** by reductive elimination.

These results require that at least 50% of the metallacycle formed from **2** cannot arise from free Cp*RhL, because it would have been scavenged quite effectively by benzene in the above reaction. We must conclude that the $C_3$ fragment and rhodium atom remain associated with one another during the conversion of **2** to **3**; i.e., we are observing a true intramolecular rearrangement ($k_R$ in Scheme II). Several possible mechanisms may account for this. Among the most interesting are the formation of $\eta^2$-$\sigma$ complexes having finite lifetimes and expansion of the three-membered ring in **2** to a hydridorhodacyclobutene intermediate. Labeling studies are under way aimed at distinguishing these possibilities and at seeking C–H to C–C activation rearrangements in other (hopefully less highly strained) systems.

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**Supplementary Material Available:** NMR spectral data for **2–5**, mass spectral, analytical, and melting point data for **3–5**, and X-ray diffraction data as discussed in the text and a crystal packing diagram (27 pages). Ordering information is given on any current masthead page.

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(7) This rearrangement is analogous to that observed with some cyclopropylhaloplatinum complexes. Philips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1970**, 1733.

(8) The orientation of the $^2H$ atom at position C-2 was determined by a combination of difference NOE and spin-decoupling techniques. We are grateful to Prof. R. H. Grubbs for suggesting these experiments.

(9) A referee has raised the possibility that this reaction may occur by addition of hydride to the metal, leading to a hydridoallylrhodium complex, followed by rearrangement to the metallacycle. We cannot rule this out in the rhodium system. However, in the corresponding $(C_5Me_5)(PMe_3)Ir$ series, we have been able to prepare and isolate the $\pi$-allyl cation, as well as the $\pi$- and $\sigma$-allyl hydrido complexes. The cation mimics its rhodium analogue in generating metallacyclobutane on treatment with $H^-$; the hydrido allyl complexes do not rearrange to the metallacycle under the $H^-$ reaction conditions and so cannot be intermediates (McGhee, W. D.; Bergman, R. G., unpublished results).

(10) A small amount of toluene was also added to keep the solution from freezing; the toluene concentration was kept low enough that the amount of hydridotolylrhodium complex formed was negligible.

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## Observation of Two Oxygen Isotope Sensitive Bands in the Low-Frequency Resonance Raman Spectrum of Oxy(phthalocyanato)iron(II)

K. Bajdor, H. Oshio, and K. Nakamoto*

*Todd Wehr Chemistry Building, Marquette University*
*Milwaukee, Wisconsin 53233*

*Received July 2, 1984*

Resonance Raman (RR) spectroscopy has been employed extensively to study the nature of bound dioxygen in oxyhemoglobin ($HbO_2$), oxymyoglobin ($MbO_2$), and their model compounds.[1] In 1974, Brunner[2] made the first observation of the $\nu(Fe–O_2)$ ($\nu$, stretch) of $HbO_2$ at 567 $cm^{-1}$ with 488-nm excitation. Since then, his assignment has been tacitly assumed to explain the cooperativity of oxygen binding[3,4] and the splitting of the $\nu(O_2)$ in IR spectra[5] as well as to confirm the end-on coordination of dioxygen in $HbO_2$.[6] Similarly, the 537-$cm^{-1}$ band of $CoHbO_2$ was assigned to the $\nu(Co–O_2)$.[7] Recently, this assignment was questioned by Benko and Yu[8] on the basis of the "zigzag" isotope shift pattern which was similar to those observed for the $\delta$(FeCO) (578 $cm^{-1}$) ($\delta$, bending) of HbCO and the $\delta$(FeNO) (551 $cm^{-1}$) of HbNO.[8] They propose to assign the 567-$cm^{-1}$ band to the $\delta$(FeOO) rather than the $\nu(Fe–O_2)$. However, they were not able to observe the second oxygen isotope sensitive band which should correspond to the $\nu(Fe–O_2)$. In fact, no workers have thus far observed two oxygen isotope sensitive bands in the low-frequency spectra of oxyhemoproteins. In this communication, we report such an observation in the RR spectra of oxy(phthalocyanato)iron(II), $Fe(Pc)O_2$, and present evidence that provides support for the original assignment by Brunner.

The experimental techniques used for the measurements of RR spectra of $Fe(Pc)O_2$ in $O_2$ matrices at ~15 K have already been reported.[9] The 676.4-nm line of Kr ion laser was used for excitation. The accuracy of frequency reading was ±1 $cm^{-1}$. In contrast with the recent report on $Fe(TPP)O_2$,[9] laser irradiation of $Fe(Pc)O_2$ did not produce the ferryl species. Although the $\nu(O_2)$ of $Fe(Pc)O_2$ was observed in IR spectra,[10] it was not observed in

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(1) For example, see: Spiro, T. G. In "Iron Porphyrins"; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: Reading, MA, 1983; Part II, p 91.

(2) Brunner, H. *Naturwissenschaften* **1974**, *61*, 129.

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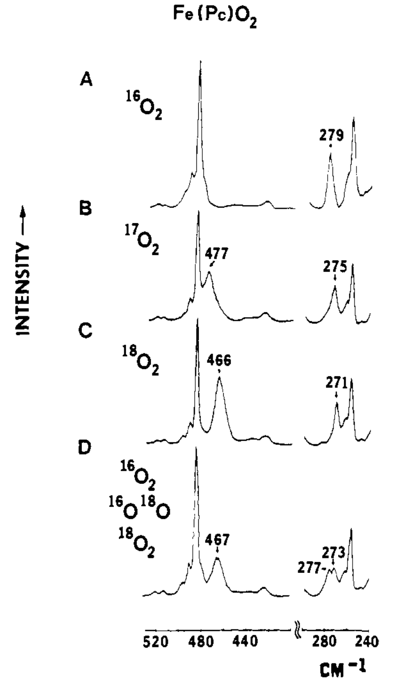

**Figure 1.** RR spectra of the Fe(Pc)$O_2$ in $O_2$ matrices at ~15 K (676.4-nm excitation, ~10 mW). The $^{17}O_2$ and $^{18}O_2$ gases used were ~77% and ~98% pure, respectively.

RR spectra as is the case for all other oxyhemoproteins.[1]

Figure 1A shows the RR spectrum of Fe(Pc)$^{16}O_2$ in pure $^{16}O_2$ matrices. The strong band at 486 cm$^{-1}$ and the medium-intensity band at 258 cm$^{-1}$ are due to Fe(Pc) vibrations. However, the band at 279 cm$^{-1}$ is shifted to 275 cm$^{-1}$ by $^{16}O_2$–$^{17}O_2$ substitution (Figure 1B). In addition, this substitution produced a new band at 477 cm$^{-1}$. Further experiments with $^{18}O_2$ (Figure 1C) shifted these bands to 271 and 466 cm$^{-1}$, respectively. These results clearly indicate that, in Fe(Pc)$^{16}O_2$, the band corresponding to those at 477 cm$^{-1}$ of Fe(Pc)$^{17}O_2$ and at 466 cm$^{-1}$ of Fe(Pc)$^{18}O_2$ is hidden under the strong Fe(Pc) band at 486 cm$^{-1}$. Figure 1D shows the RR spectrum of Fe(Pc) cocondensed with a mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ in the 1:2:1 ratio. In this case, two bands are observed at around 277 and 273 cm$^{-1}$.

In order to assign the oxygen isotope sensitive bands, we have carried out normal coordinate calculations on a triatomic Fe–$O_I$–$O_{II}$ system. According to Jameson et al.,[11] the Fe–$O_I$ ($R_1$) and $O_I$–$O_{II}$ ($R_2$) distances and Fe–$O_I$–$O_{II}$ angle ($\alpha$) of Fe($O_2$)($T_{piv}$PP)(2-MeIm)EtOH are 1.90 Å, 1.22 Å, and 129°, respectively. Since no X-ray data are available on Fe(Pc)$O_2$, we varied the molecular dimensions through the following values: $R_1$ = 1.90–2.00 Å, $R_2$ = 1.22–1.25 Å, and $\alpha$ = 129–137.5°. Table I shows the results obtained for $R_1$ = 2.00 Å, $R_2$ = 1.25 Å, and $\alpha$ = 137.5°. The set of force constants used was $K(R_1)$ = 1.90, $K(R_2)$ = 6.58, and $H(\alpha)$ = 0.22 (all in units of mdyn/Å). Slight changes in force constants gave similar good fits when the molecular dimensions were varied in the above ranges. Most importantly, the potential energy distribution calculations show that for the above set of parameters, the band near 490 cm$^{-1}$ is 70% $\nu$(Fe–$O_2$) and 27% $\delta$(FeOO), while the band near 280 cm$^{-1}$ is 72% $\delta$(FeOO) and 25% $\nu$(Fe–$O_2$). However, the degree of mixing decreases as $\alpha$ increases. At the reported angle of 156° for Hb$O_2$,[12] the ~490- and ~280-cm$^{-1}$ bands become ~90% pure $\nu$(Fe–$O_2$) and $\delta$(FeOO), respectively. Only the use of unreasonably small $K(R_1)$ values (~1.1 mdyn/Å) can reverse these assignments (cf. $K(R_1)$ = 3.08 mdyn/Å of Hb$O_2$[6]).

As shown in Table I, normal coordinate calculations predict the frequency order of the $\nu$(Fe–$O_2$) rather than the $\delta$(FeOO)[8] to be $Fe^{16}O^{16}O > Fe^{18}O^{16}O < Fe^{16}O^{18}O > Fe^{18}O^{18}O$. In fact, the $\delta$(FeOO) should exhibit a gradual decrease in the above order of isotopic substitution. These trends are entirely opposite to those found for the Fe–CO system.[13] The difference arises because the Fe–CO bond is linear and the central atom (C) is lighter than the terminal atom (O).

**Table I.** Comparison of Observed and Calculated Frequencies (cm$^{-1}$)

| | | $\nu(O_2)$ | $\nu$(Fe–$O_2$) | $\delta$(FeOO) |
|---|---|---|---|---|
| (Pc)$Fe^{16}O^{16}O$ | obsd | 1207 | 488[a] | 279 |
| | calcd | 1209 | 490 | 281 |
| (Pc)$Fe^{16}O^{18}O$ | obsd | 1176 | 487[a,b] | 273[b] |
| | calcd | 1178 | 486 | 273 |
| (Pc)$Fe^{18}O^{16}O$ | obsd | 1176 | 467[c] | 277[e] |
| | calcd | 1172 | 470 | 277 |
| (Pc)$Fe^{18}O^{18}O$ | obsd | 1144 | 466 | 271 |
| | calcd | 1140 | 467 | 269 |
| (Pc)$Fe^{17}O^{17}O$ | obsd | | 477 | 275 |
| | calcd | 1173 | 478 | 275 |

[a] Expected value. [b] Overlap with $\nu$(Fe–$^{16}O_2$). [c] Overlap with $\nu$(Fe–$^{18}O_2$). [d] Overlap with $\delta$($Fe^{18}O^{18}O$). [e] Overlap with $\delta$($Fe^{16}O^{16}O$).

The $\nu$(Fe–NO) and $\delta$(FeNO) of $Fe^{III}$MbNO are at 595 and 573 cm$^{-1}$, respectively, in solution.[8] These frequencies are close to that of Fe(Pc)NO (580 and 567 cm$^{-1}$) in a NO matrix at ~15 K.[14] The $\nu(O_2)$ of Hb$O_2$ is ~1130 cm$^{-1}$ in solution,[5] whereas that of Fe(Pc)$O_2$ in an $O_2$ matrix is 1207 cm$^{-1}$.[10] In general, the higher the $\nu(O_2)$, the lower the $\nu$(metal–$O_2$).[15] Hence, the lowering of the $\nu$(Fe–$O_2$) in going from Hb$O_2$ (567 cm$^{-1}$) to Fe(Pc)$O_2$ (488 cm$^{-1}$) is anticipated. These results suggest that the nature of metal–oxygen bonding in the above two compounds does not differ markedly in spite of appreciable differences in their environments.

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# Trisubstituted Heteropolytungstates as Soluble Metal Oxide Analogues. 1. The Preparation, Characterization, and Reactions of Organic Solvent Soluble Forms of $Si_2W_{18}Nb_6O_{77}^{8-}$, $SiW_9Nb_3O_{40}^{7-}$, and the $SiW_9Nb_3O_{40}^{7-}$ Supported Organometallic Complex $[(C_5Me_5)Rh{\cdot}SiW_9Nb_3O_{40}]^{5-}$

Richard G. Finke* and Michael W. Droege

*Department of Chemistry, University of Oregon*
*Eugene, Oregon 97403*

*Received June 1, 1984*

Development of polyoxoanions[1a] as discrete, soluble metal oxide analogues[2] has been hampered by the limited number of polyoxoanions containing sufficient charge density at their surface oxygens[1b] to covalently bind transition-metal catalysts. Furthermore, almost nothing is known about how multiple V-, Nb-,

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