termediate $OOCl^-$ leaves a spin-paired oxygen molecule, thus a singlet excited state.[17] Catalase, however, functions chiefly in the decomposition of hydrogen peroxide to molecular oxygen without the presence of halogen ion cofactors, and in this system, a bound singlet molecular oxygen is generated predominantly, which then radiatively decays either directly as a perturbed species or via an energy-transfer mechanism.

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Rearrangement of Bridging Alkylidyneiron Complexes to Bridging Alkenyliron Complexes

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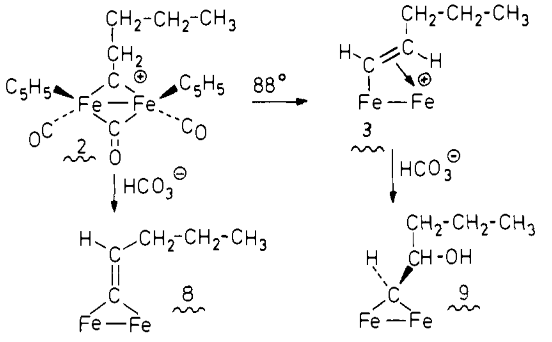
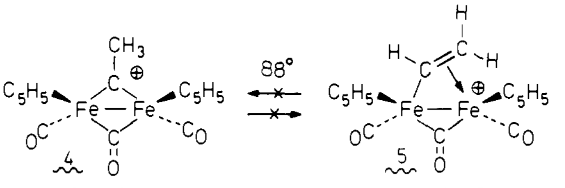
The electrophilic diiron methylidyne complex $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CH)]^+PF_6^-$ (**1**)[1] reacts rapidly with alkenes by adding the methylidyne C–H bond across the C=C double bond to produce μ-alkylidyne complexes.[2] In the course of examing the possibile reversibility of this hydrocarbation reaction, we found that μ-alkylidyne complexes rearrange to μ-alkenyl complexes in a reaction whose rate is extremely sensitive to the degree of alkyl substitution at the carbon α to the carbyne carbon.

When the μ-pentylidyne complex $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C\text{–}CH_2CH_2CH_2CH_3)]^+PF_6^-$ (**2**)[3,4] was heated in the solid state or in dilute CD_2Cl_2 solution, no (<5%) reversal to 1-butene and **1** was detected. Instead, upon heating to 88 °C for 29 h, solid **2** rearranged to the μ-1-pentenyl complex $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH_2CH_2CH_3)]^+PF_6^-$(**3**)[4] in 89% yield after recrystallization.[7] The rearrangement of **2** to **3** in CD_2Cl_2 at 88.0 ± 0.1 °C was followed by ^1H NMR observation of the Cp resonances; the first-order rate constant was found to be $2.9 \pm 0.5 \times 10^{-4}\ s^{-1}$ which corresponds to $\Delta G^\ddagger = 27.1 \pm 0.2$ kcal. Rearrangement of the related α-deuterated compound $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C\text{–}CD_2CH_2CH_2CH_3)]^+CF_3SO_3^-$ (**2**-d_2)[8] gave $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CD{=}DCCH_2CH_2CH_3)]^+CF_3SO_3^-$ (**3**-d_2) in which >95% of the deuterium was located in the vinylic sites as established by ^2H NMR; this indicates that the net 1,2-hydride shift involves only the protons on the carbon α to the carbyne carbon of **2**.



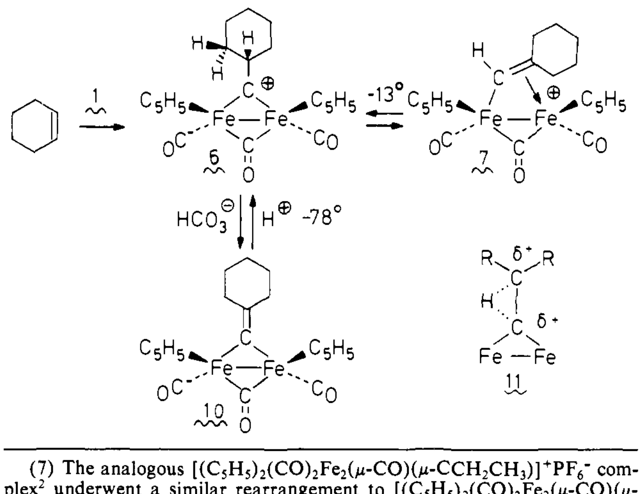


The structure of **3** was established spectroscopically.[4] Separate signals are seen for the nonequivalent C_5H_5 rings of **3** in the low-temperature ^1H NMR at δ 5.83 and 5.62 and in the low-temperature ^{13}C NMR at δ 92.6 and 89.8; at room temperature a fluxional process leads to single coalesced peaks.[9] The proton on the α-vinyl carbon of **3** appears characteristically downfield at δ 12.06 (d, $J_{trans} = 11.8$ Hz) and the proton of the β-vinyl carbon appears as a multiplet at δ 3.66. In the ^{13}C NMR of **3**, the α- and β-vinyl carbons appear at δ 175.4 and 96.7. Similar spectra for μ-vinyl compounds have been observed by Pettit[6] and Dyke.[10]

In contrast, attempted rearrangement of the parent ethylidyne complex **4**[5,6] by heating at 88 °C for 100 h gave no detectable isomerization (<5%) to μ-vinyl complex **5** but led to 50% decomposition. When the potential rearrangement product **5**[6,10] was independently synthesized and heated at 88 °C for 20 h, no ethylidyne complex **4** was observed but 80% decomposition of **5** had occurred. Apparently, an α-alkyl substituent on the μ-alkylidyne complexes can greatly accelerate the rearrangement to a μ-alkenyl complex.

The possibility that two α-alkyl substituents might further accelerate the rearrangement of μ-alkylidyne complexes to μ-alkenyl complexes caused us to reassess our interpretation of the reaction of **1** with 1,2-disubstituted alkenes. Earlier we had found that cyclohexene, cyclopentene, and *cis*- and *trans*-2-butene all reacted with **1** to give mixtures of μ-alkylidyne complexes and μ-alkenyl complexes. We postulated that the μ-alkylidyne complexes were formed by direct 1,2-addition of the CH bond of **1** to the alkene and that the μ-alkenyl complexes were formed via a hydrogen migration of an intermediate carbocation.[11] If these two products rapidly interconvert either might be the initial product of reaction of the 1,2-disubstituted alkene with **1**.

When the 1.4:1.0 mixture of μ-alkylidyne **6** and μ-alkenyl **7** complexes obtained from reaction of **1** with cyclohexene was heated at 88 °C in the solid state or in CD_2Cl_2 solution, no change in isomer ratio was seen. Even when partial decomposition



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[1] Casey, C. P.; Fagan, P. J.; Miles, W. M. *J. Am. Chem. Soc.* **1982**, *104*, 1134-1136.

[2] Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4950-4951.

[3] **2** was prepared by the reaction of **1** with 1-butene in 76% yield or by reaction of *n*-BuLi with $(C_5H_5)_2(CO)_4Fe_2$ followed by acidification with aqueous HPF_6 in 26% yield.[5,6]

[4] See supplementary material for full spectral and analytical characterization.

[5] Nitay, M.; Priester, W.; Rosenblum, M. *J. Am. Chem. Soc.* **1978**, *100*, 3620-3622.

[6] Kao, S. C.; Lu, D. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911-918.

[7] The analogous $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_3)]^+PF_6^-$ complex[2] underwent a similar rearrangement to $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}CHCH_3)]^+PF_6^-$ (84% yield, ≥95% conversion) upon heating at 88 °C for 30 h in the solid state.

[8] **2**-d_2 was prepared by deuterium exchange of the vinylic protons of **8** using CF_3COOD/D_2O. The product **8**-d_1 was protonated with CF_3SO_3D yielding **2**-d_2 in 49% yield for the two steps.

[9] Casey, C. P.; Marder, S. R., unpublished results.

[10] Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1980**, 441-442; *J. Chem. Soc., Dalton Trans.* **1983**, 1417.

[11] In contrast, 1-methylcyclohexene reacts with **1** to give a μ-alkenyl compound via exclusive carbon migration.[2]

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occurred, the 1.4:1.0 ratio of **6**:**7** did not change perceptibly. These results are consistent with a very rapid isomerization that maintained an equilibrium mixture of the compounds or with no isomerization at all as seen in the case of μ-ethylidyne complex **4**.

Aqueous HCO_3^- reacts rapidly with μ-pentylidyne complex **2** to produce the μ-pentenylidene complex **8**[4] in 87% yield whereas the μ-pentenyl complex **3** reacts only slowly with HCO_3^- over 24 h to give the β-hydroxy bridging carbene complex **9**[4] in 47% yield. Therefore it appeared possible that a pure sample of μ-alkenyl complex **7** might be obtained by selectively destroying μ-alkylidyne complex **6** by treatment with base. However, when the 1.4:1.0 mixture of **6** and **7** was treated with aqueous bicarbonate, all of the material was rapidly converted to the same vinylidene complex **10** which was isolated in 70% yield. The fact that both **6** and **7** were converted to **10** is consistent with a rapid equilibration of **6** and **7** at room temperature and selective deprotonation of **6** to **10**.[12] This deprotonation reaction could prove useful for converting synthetically unattractive mixtures of products from the reaction of **1** with 1,2-disubstituted alkenes into a single organometallic product.

Vinylidene complexes such as **8** are known to undergo protonation to give μ-alkylidyne complexes and not μ-alkenyl compounds.[6,13] When the cyclohexyl vinylidene complex **10** was reprotonated with $HBF_4 \cdot Et_2O$ in acetone-d_6 at −70 °C, only the BF_4^- salt of the cyclohexyl-substituted carbyne complex **6** was observed by ^1H NMR. Upon warming to −13 °C, pure **6** was converted to a 1.4:1.0 equilibrium mixture of **6**:**7**.[14] The rate of rearrangement of **6** to **7** was measured by ^1H NMR observation of the Cp resonances; the first-order rate constant for conversion of **6** to an 1.4:1 equilibrium mixture of **6**:**7** was found to be $k_e = 2.4 \pm 1.0 \times 10^{-4}\ s^{-1}$. The rate constant for conversion of **6** to **7** is given by $k = k_e(1 + K_{eq}^{-1})^{-1} = 1.0 \pm 0.4 \times 10^{-4}\ s^{-1}$, which corresponds to $\Delta G^‡ = 19.9 \pm 0.3$ kcal. Since we now know that the μ-alkylidyne and μ-alkenyl products **6** and **7** rapidly equilibrate, additional experiments will be required to determine the nature of the kinetic product from the reaction of **1** with 1,2-disubstituted alkenes.

The rate of rearrangement of μ-alkylidyne complexes to the corresponding μ-alkenyl complexes is increased dramatically by carbon substituents on the carbon α to the carbyne carbon. Thus, **4** with no α-carbon substituents does not rearrange at 88 °C ($\Delta G^‡ \geq 31.0$ kcal), **2** with one α-carbon substituent rearranges slowly at 88 °C ($\Delta G^‡ = 27.1 \pm 0.2$ kcal), and **6** with two α-carbon substituents rearranges rapidly at −13 °C ($\Delta G^‡ = 19.9 \pm 0.3$ kcal). This reactivity pattern suggests the buildup of positive charge at the carbon α to the carbyne carbon at the transition state for rearrangement; a transition state such as **11** is consistent with this reactivity pattern.

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Supplementary Material Available: Spectral and analytical characterizations of compounds indicated by ref 4 (2 pages). Ordering information is given on any current masthead page.

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[12] Similar aqueous HCO_3^- treatment of the 2.3:1.5:1.0 mixture of $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CCH(CH_3)CH_2CH_3)]^+PF_6^-$, $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(Z)\text{-}CH{=}C(CH_3)CH_2CH_3)]^+PF_6^-$, and $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}(E)\text{-}CH{=}C(CH_3)CH_2CH_3)]^+PF_6^-$ obtained from reaction of *cis*-2-butene with **1** gave complete conversion to $(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CH_3)CH_2CH_3)$, which was isolated in 58% yield. Reprotonation with $HBF_4 \cdot O(CH_2CH_3)_2$ regenerated the BF_4^- salts in the 2.3:1.5:1.0 ratio in 47% yield.

[13] (a) Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Plaas, D.; Taylor, G. E. *J. Organomet. Chem.* **1980**, *198*, C43–49. (b) Dawkins, G. M.; Green, M.; Jeffery, J. C.; Sanbale, C.; Stone, F. G. A. *J. Chem. Soc. Dalton Trans.* **1983**, 499–506.

[14] When the sample was observed at −70 °C only the alkylidyne Cp's of **6** at δ 5.76 were observed. Upon warming to −13 °C both the alkylidyne Cp's of **6** at δ 5.76 and the μ-alkenyl Cp's at δ 5.68 were observed. The vinylic proton of **7** and the proton on the carbon α to the carbyne carbon of **6** were not observed by ^1H NMR presumably due to prior deuterium exchange of $HBF_4 \cdot O(CH_2CH_3)_2$ with $(CD_3)_2CO$.

Artificial Transaminase Carrying a Synthetic Macrocyclic Binding Group

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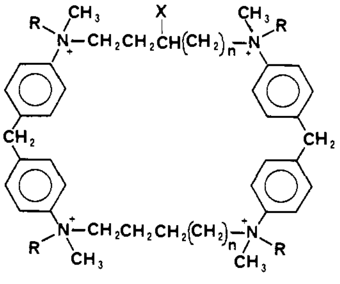
Although various catalysts based on cyclodextrin binding groups[4] have been successful as enzyme mimics, it is obviously desirable to generalize them by using synthetic binding cavities. A number of macrocycles have been prepared that exhibit hydrophobic properties; of these, the systems such as **1**, described by Koga[5] (based on earlier work by Stetter[6]) are particularly attractive because an X-ray structure determination[5] shows that a bound substrate, durene, is indeed located in the cavity. Since **1** dissolves and binds small hydrophobic molecules only in strong acid solution, we have prepared its quaternary derivative[7] **2** and find that **2** binds 2,7-dihydroxynaphthalene in neutral solution with upfield shifting of the ^1H NMR signals very similar (upfield shifting by 1.53, 0.48, and 1.34 ppm for H-1(8), H-3(6), and H-4(5), with 25 mM **2**, for 12.5 mM dihydroxynaphthalene in neutral D_2O) to those (upfield shifting by 1.36, 0.56, and 1.31 ppm for 25 mM dihydroxynaphthalene in D_2O/DCl) for Koga's complex. The dissociation constant for binding 8-anilino-1-naphthalenesulfonate (ANS), from a Hildebrand–Benesi plot[8] of fluorescence at 25 °C, was 6.6×10^{-5} M for **2** in neutral H_2O, compared with a reported 1.6×10^{-4} M for **1** in acid. Thus it is clear that **2** also binds substrates inside its cavity.



1 n = 1; R = H; X = H

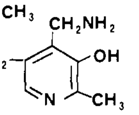
2 n = 1; R = CH_3; X = H

3 n = 2; R = CH_3; X = H

4 n = 2; R = H; X = H

5 n = 2; R = CH_3; X = $SCOCH_3$

6 n = 2; R = CH_3; X = SCH_2–



Similarly, we have prepared macrocycle **3**, analogous to Koga's **4**, and find that K_{diss} is 8.4×10^{-5} M for the complex of **3** with

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[2] On leave from the University of Thessalonika, 1980–1981.

[3] NATO Postdoctoral Fellow, 1982–1983.

[4] For recent reviews, see: Breslow, R. *Science* (*Washington, D.C.*) **1982**, *218*, 532. Tabushi, I. *Acc. Chem. Res.* **1982**, *15*, 66.

[5] (a) Odashima, K.; Itai, A.; Iitaka, Y.; Koga, K. *J. Am. Chem. Soc.* **1980**, *102*, 2504. (b) Odashima, K.; Soga, T.; Koga, K. *Tetrahedron Lett.* **1981**, 5311.

[6] Stetter, H.; Roos, E.-E. *Chem. Ber.* **1955**, *88*, 1390.

[7] Satisfactory ^1H NMR and CI-MS data were obtained for all new compounds. In the case of the quaternized macrocycles, clean molecular ions could not be obtained by using field-desorption mass spectroscopy, so **2** was analyzed. Anal. Calcd for $C_{42}H_{60}N_4I_4$ (Found): C, 44.69 (44.69); H, 5.37 (5.50); N, 4.97 (4.90); I, 44.97 (44.69). **6** was analyzed as a pentabicarbonate. Anal. Calcd for $C_{57}H_{80}N_6SO_{16} \cdot 7H_2O$ (Found): C, C, 54.18 (54.46); H, 7.50 (7.42); N, 6.65 (6.87).

[8] Hildebrand, J. A.; Benesi, H. A. *J. Am. Chem. Soc.* **1949**, *71*, 2703.

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