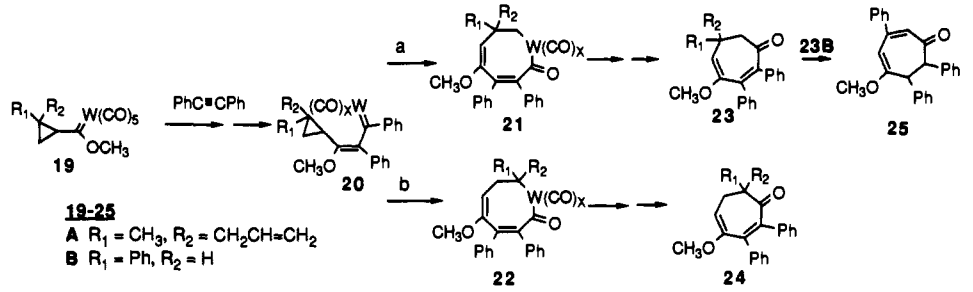
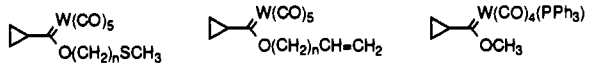
Scheme V



yields were generally higher when triarylphosphines were present in the reaction, but the reaction was severely retarded by more nucleophilic phosphines like (diphenylphosphino)ethane and tributylphosphine. Triphenylphosphine-substituted complex **11** was considerably less reactive than pentacarbonyl complex **4**,[6] suggesting that phosphines assist with some later stage of the reaction, but are detrimental if initial CO-ligand replacement occurs. Contrary to our predictions, complexes **7-10** were as unreactive as the parent carbene complex **4** in reactions with diphenylacetylene.[7]



7 n = 2
8 n = 3

9 n = 2
10 n = 3

11

The reaction proceeded similarly with 4-octyne or 1-phenylpropyne at 140 °C to produce isomerized cycloheptadienone derivatives (**12** + **13**) in 61% (**12A**:**13A** = 85:15) and 45% (only **12B**) yields, respectively (Scheme III). With 1-phenylpropyne, only the indicated regioisomer was obtained.[5,8] In these two cases, substantial amounts of furanones (**14**) were obtained when a phosphine additive was omitted.[9] Terminal alkynes did not provide cycloheptadienone derivatives. Upon thermolysis, alkyne-carbene complex **15** produced cycloheptadienone derivative **17** in 63% yield (Scheme IV). Cycloheptadienone **17** is presumably the thermodynamically more stable compound, perhaps due to an anomeric effect.[10] At long reflux times (>20 h), hydrogenated compound **18** was a significant impurity.

Carbene complexes containing unsymmetrical cyclopropane rings can lead to two possible cycloaddition products (Scheme V). Reaction of diphenylacetylene with complex **19A** led to only cycloheptadienone **23A** in 30% yield; with (phenylcyclopropyl)carbene complex **19B**, cycloheptadienone **25** was produced in 53% yield. The observed regiochemistry reflects a preference for breaking the less-substituted carbon-carbon bond of the cyclopropane ring in the ring-opening step,[2a,11] eventually giving the compound wherein tungsten is bonded to the less-substituted carbon in intermediate metallacycle **21** (path a). The reaction is obviously driven by steric effects since the activating effect of a phenyl ring should have driven the reaction toward pathway b.[13]

In summary, we have discovered a new cycloaddition reaction for the synthesis of seven-membered rings. The reaction shows regioselectivity both in the alkyne addition steps and in the cyclopropane ring opening steps and is a potentially powerful synthetic method. Further investigations in the areas of yield optimization and delineation of the differences in behavior of different cyclopropane-substituted metal-carbene complexes are ongoing.

Acknowledgment. This research was supported by grants from the National Institutes of Health (GM-40777) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (23332-AC1).

Supplementary Material Available: Complete experimental procedures and characterization for all key compounds including ^1H and ^{13}C NMR, IR, and mass spectral data and ^1H and ^{13}C NMR spectra (29 pages). Ordering information is given on any current masthead page.

(6) For *alkyl*carbene-chromium complexes, the triphenylphosphine-substituted complexes are more reactive. Xu, Y.-C.; Wulff, W. D. *J. Org. Chem.* **1987**, *52*, 3263-3275.

(7) For a successful application of this approach, see: Dötz, K. H.; Erben, H.-G.; Harms, K. *J. Chem. Commun.* **1989**, 692-693.

(8) (a) Wulff, W. D.; Tang, P.-C.; McCallum, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 7677-7678. (b) Dötz, K. H.; Dietz, R. *Chem. Ber.* **1977**, *110*, 1555-1563.

(9) Furans and furanones are often byproducts in the reaction between Fischer carbene complexes and alkynes. McCallum, J. S.; Kunng, F. A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346-2360.

(10) See: Venkataraman, H.; Cha, J. K. *Tetrahedron Lett.* **1989**, *30*, 3510-3513 and references therein.

(11) For a recent reference to mechanistic studies of the reaction between alkynes and Fischer carbene complexes, see: Anderson, B. A.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 8615-8617. An alternative mechanistic pathway has been suggested by a reviewer: the reaction produces (cyclopropylvinyl)ketene intermediate, which undergoes electrocyclic ring closure to generate a cycloheptadienone. This mechanism is probably not operative since 4-cyclopropyl-4-methoxy-2,3-diphenyl-2-cyclobutenone and 4-cyclopropyl-4-hydroxy-2,3-diisopropoxy-2-cyclobutenone both fail to produce seven-membered rings upon thermolysis.[12] Metal-complexed vinylketenes, however, cannot be ruled out as intermediates.

(12) For a recent reference to this chemistry, see: Danheiser, R. L.; Brisbois, R. G.; Kowalczyk, J. J.; Miller, R. F. *J. Am. Chem. Soc.* **1990**, *112*, 3093-3110 and references therein.

(13) This is an example of a donor-acceptor-activated cyclopropane, and thus the ring should open as in path b. Reissig, H.-U. *Top. Curr. Chem.* **1988**, *144*, 73-136.

Catalytic Disproportionation of Hydrogen Peroxide by $[Mn^{IV}(\mu_2\text{-}O)(SALPN)]_2$

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Functional modeling of the reactions performed by the manganese catalase and the oxygen evolving complex are scarce although two systems which catalytically convert hydrogen peroxide to dioxygen and water have been described. The first[1] employs a dimanganese Schiff base complex which cycles between Mn^{II}_2 and Mn^{III}_2 while the second[2] uses a Mn(III) porphyrin dimer that may achieve the Mn(IV) or Mn(V) oxidation level during catalysis. Although groundbreaking in their ability to catalyze this important reaction, neither system contains the biologically precedented $(\mu_2\text{-}O^{2-})_2$ core. Previously, models having this structural unit have not exhibited catalase activity.[1] We have described[4] the quantitative formation of $[Mn^{IV}(SALPN)(\mu_2\text{-}O)]_2$ (**1**) by the reaction of [bis(salicylideneaminato)propane][acetonylacetonate]manganese(III), (Mn^{III}(SALPN)(AcAc)) with hy-

(1) Mathur, P.; Crowder, M.; Dismukes, G. C. *J. Am. Chem. Soc.* **1987**, *109*, 5227-5233.

(2) Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1991**, *113*, 3595-3596.

(3) Waldo, G. S.; Penner-Hahn, J. E., manuscript to be submitted.

(4) Larson, E. J.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1991**, *113*, 3810.

(5) Larson, E. J.; Riggs, P.; Penner-Hahn, J. E.; Pecoraro, V. L. Submitted to *J. Chem. Soc., Chem. Commun.*

(6) Stibrany, R. T.; Gorun, S. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, No. 10, 1156.

(7) Cofré, P.; Sawyer, D. T. *Inorg. Chem.* **1986**, *25*, 2089-2092.

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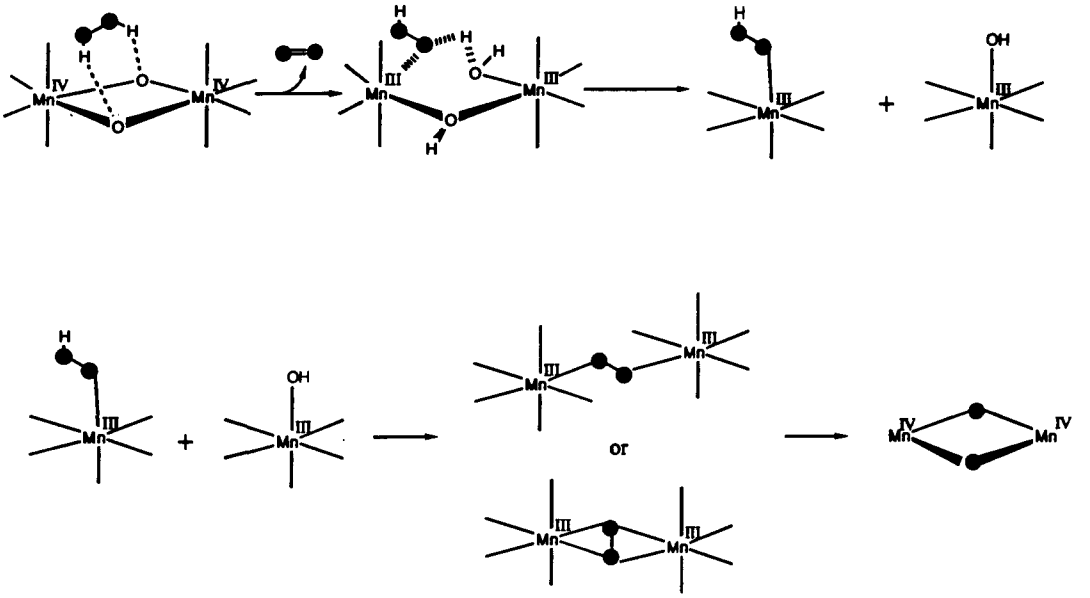

Figure 1. One minimal pathway for hydrogen peroxide decomposition catalyzed by **1** that is consistent with data presented herein and in ref 4. The first step is oxidation of hydrogen peroxide to dioxygen and concomitant reduction of **1** to the Mn(III) oxidation level. A monomeric Mn(III) species[4] can then react with a second equivalent of hydrogen peroxide to incorporate label into the bridging oxide positions.

drogen peroxide. Herein we demonstrate that **1** can efficiently complete the catalase reaction[8] for 1000 turnovers without catalyst decomposition and with resultant oxygen isotope composition identical to the manganese catalase of *Lactobacillus plantarum*.

The dimer **1** was prepared as described previously[4] as either the $[Mn^{IV}(SALPN)(\mu_2\text{-}^{16}O)]_2$, $\{(\mu_2\text{-}^{16}O)\text{:}\mathbf{1}\}$, or $[Mn^{IV}(SALPN)(\mu_2\text{-}^{18}O)]_2$, $\{(\mu_2\text{-}^{18}O)\text{:}\mathbf{1}\}$, forms. Isotopic composition was confirmed using negative ion FAB mass spectrometry monitoring MW 702 and 706, respectively. Catalase reactions were completed in dichloromethane by the addition of $\approx$1 mM H_2O_2 solutions in acetonitrile.[9] Turnover of hydrogen peroxide to yield dioxygen was monitored by manometry and shown to be quantitative in less than 1 min using as much as 1000-fold molar excess H_2O_2. Greater than 90% of the starting catalyst was recovered. The dioxygen isotope composition was analyzed by mass spectroscopy. The reaction of $\{(\mu_2\text{-}^{16}O)\text{:}\mathbf{1}\}$ with $H_2{}^{18}O_2$ yielded exclusively $^{18}O_2$, while the reverse combination $\{(\mu_2\text{-}^{18}O)\text{:}\mathbf{1}\}$ and $H_2{}^{16}O_2$ gave the expected $^{16}O_2$.[10] This demonstrates that dioxygen derived exclusively from hydrogen peroxide and not from the μ_2-oxo linkages of the dimer. The reaction of $\{(\mu_2\text{-}^{16}O)\text{:}\mathbf{1}\}$ with a 1:1 mixture of $H_2{}^{16}O_2$ and $H_2{}^{18}O_2$ gave a mixture of $^{16}O_2$ and $^{18}O_2$ with only the predicted statistical distribution of $^{16,18}O_2$ based on residual $H_2{}^{16,18}O_2$. Thus, both oxygen atoms of dioxygen must come from the *same* hydrogen peroxide molecule. This isotope labeling pattern is identical to that seen for the *L. plantarum* Mn catalase.[3]

Oxidation of $Mn^{III}(SALPN)(AcAc)$ or $[Mn^{III}(SALPN)(OCH_3)]_2$ with $H_2{}^{18}O_2$ gives exclusively $\{(\mu_2\text{-}^{18}O)\text{:}\mathbf{1}\}$.[4] In these cases, both bridging oxo groups originated from the same peroxide molecule and scrambling of labeled SALPN was observed. These results implicated a monomeric hydroperoxy Mn(III) intermediate. We reasoned that similar chemistry might be operative in the catalase reactions.

The isotopic composition of **1** recovered from the catalase experiments showed substantial enrichment of label into the $\mu_2\text{-}O^{2-}$. Reactions completed under high dilution conditions[11] using a 4:1 ratio of $H_2{}^{18}O_2$ and $\{(\mu_2\text{-}^{16}O)\text{:}\mathbf{1}\}$ gave predominantly (>95%) $\{(\mu_2\text{-}^{18}O)\text{:}\mathbf{1}\}$, demonstrating that the $\mu_2\text{-}O^{2-}$ ligands are extensively exchanged during the course of the reaction. A 30%:70% mixture of $H_2{}^{16}O_2$:$H_2{}^{18}O_2$ in a 4-fold excess over $\{(\mu_2\text{-}^{16}O)\text{:}\mathbf{1}\}$ gives $\{(\mu_2\text{-}^{16}O_2)\text{:}\mathbf{1}\}$ and $\{(\mu_2\text{-}^{18}O)\text{:}\mathbf{1}\}$ in the isotopic ratio of the added peroxide (30%:70%), but no increase in $[Mn^{IV}(SALPN)(\mu_2\text{-}^{16,18}O)]_2$. The reaction of a 1:1 mixture of $[Mn^{IV}(SALPN)(\mu_2\text{-}O)]_2$ and $[Mn^{IV}(3,5\text{-}Cl_2\text{-}SALPN)(\mu_2\text{-}O)]_2$ with hydrogen peroxide gave a mixture of $[Mn^{IV}(SALPN)(\mu_2\text{-}O)]_2$, $[Mn^{IV}(SALPN)(3,5\text{-}Cl_2\text{-}SALPN)(\mu_2\text{-}O)]_2$, and $[Mn^{IV}(3,5\text{-}Cl_2\text{-}SALPN)(\mu_2\text{-}O)]_2$. A 1:1 mixture of the parent $[Mn^{IV}(SALPN)(\mu_2\text{-}O)]_2$ and $[Mn^{IV}(3,5\text{-}Cl_2\text{-}SALPN)(\mu_2\text{-}O)]_2$ is stable to ligand exchange for at least 1 week[12] under these conditions in the absence of hydrogen peroxide. Therefore, the catalase reaction proceeds with exchange of the bridging oxo groups. Both the resultant μ_2-oxo atoms originate from the same peroxide molecule, and the observed scrambling of the MnL units is as predicted for a monomeric $Mn^{III}(SALPN)$ intermediate.

The observations above suggested that the first redox step of the process was initial oxidation of hydrogen peroxide to give a Mn(III) species. The electrochemistry of **1** shows irreversible, reductive electrochemistry at −150 mV vs SCE and an ill-defined, ligand-centered oxidation at +1.4 V. Under these conditions H_2O_2 is not a sufficiently strong oxidant to attack the ligand. This supports the model that the initial redox step is reduction of the dimer to a Mn(III) species which is subsequently reoxidized to **1** by a second equivalent of hydrogen peroxide. The observations described above are consistent with the reaction scheme provided as Figure 1. Notably, **1** can be protonated at the oxo bridge[5] to form $\{[Mn^{IV}(SALPN)]_2[(\mu_2\text{-}O),(\mu_2\text{-}OH)]\}^+$. In contrast to **1**, this complex is not competent in the catalase reaction.

Future experiments will focus on defining more precisely the order of each reactant and the proton dependence of the process and explaining why **1** is the first $[Mn^{IV}(\mu_2\text{-}O)]_2$ dimer which can efficiently undergo a catalase reaction.

Acknowledgment. The authors thank the NIH (GM-39406) for support of this work, Amoco Oil Company for a graduate Fellowship to E.J.L., and the Alfred P. Sloan Foundation for a Fellowship to V.L.P.

(8) Manganese ion in solution catalyzes peroxide decomposition. For comparison (rate of O_2 evolution [mL s^{-1}] with excess peroxide): $MnCl_2$, 0.01; $Mn(OAc)_2$, 0.1; solid MnO_2, 0.25 (see ref 6); **1**, 8.0–10.0 as obtained from manometry.

(9) Nonaqueous hydrogen peroxide was prepared as described in ref 7 followed by dilution in acetonitrile and titration with $KMnO_4$. Typically peroxide concentrations were around 1 mM. The above solution was added to a methylene chloride solution of **1** (around 0.2 mM).

(10) Reactions were run on a Schlenk line using initially nitrogen gas atmosphere with both peroxide and **1** solutions deoxygenated by freeze–pump–thaw cycles. A prepurged gas collection tube (obtained from Aldrich) was used to sample the resultant headspace gas which was then analyzed by using mass spectrometry.

(11) Water formed in the reaction causes aggregation and precipitation of **1** so that high dilution ($\sim$0.01 mM **1** in CH_2Cl_2) was required to observe efficient isotopic exchange at low turnover numbers.

(12) A solution containing 50:50 **1** and $[Mn^{IV}(3,5\text{-}Cl_2\text{-}SALPN)(\mu_2\text{-}O)]$ in methylene chloride shows no evidence of ligand exchange after a week at room temperature as determined by using negative ion FAB mass spectrometry.