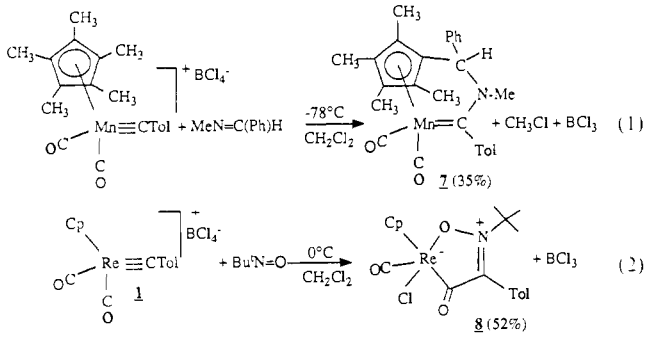

planar, and the short C(3)-N distance of 1.29 (2) Å implies a localized double bond between these atoms.

A nucleophilic substrate is evidently required for cycloaddition to occur with **1** and **2** since alkynes and olefins fail to react, even those with electron-releasing groups [e.g., CH_2=CH(OEt)]. Similarly, no reaction occurred with the imines MeN=C(Cl)Ph and MeN=C(OMe)Ph, apparently because of the reduced nucleophilicity of the nitrogen atom. Complexes **1** and **2** clearly have a rich and varied cycloaddition chemistry with unsaturated, nucleophilic organic substrates, and we anticipate potential synthetic applications of the metallacycles which derive from such reactions.

Acknowledgment. The National Science Foundation (CHE-8802025) is gratefully acknowledged for support of this research.

Supplementary Material Available: Tables of atomic positional parameters for **3** and **8** (3 pages). Ordering information is given on any current masthead page.

(15) **8**: orthorhombic, *Fdd*2, a = 21.700 (9) Å, b = 38.016 (11) Å, c = 11.120 (3) Å, V = 9166 Å^3, Z = 16. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were found and refined isotropically except for those of the methyl groups which were idealized. The phenyl ring was given rigid body constraints. A molecule of CH_2Cl_2 for each Re complex was found in the lattice. The enantiomer reported gave a multiplicative factor for $\Delta f''$ = 1.02 (5). $R(F)$ = 5.22%, $R(wF)$ = 5.76% for 3013 observed reflections at the $5\sigma(F_o)$ level. Re-Cl(1), 2.455 (5); Re-C(2), 2.07 (2); Re-O(2), 2.06 (1); C(2)-C(3), 1.53 (2); C(3)-N, 1.29 (2); N-O(2), 1.33 (2) Å. C(2)-Re-O(2), 75.7 (5); Re-C(2)-C(3), 112.7 (10); C(2)-C(3)-N, 113 (1); C(3)-N-O(2), 118 (1); N-O(2)-Re, 118.9 (8)°.

The Chemistry of Vicinal Tricarbonyls. A Stable Vinyl Tricarbonyl Hydrate as a Di- and Trielectrophile

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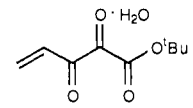
The greatly enhanced reactivity of the central carbonyl of a 1,2,3-tricarbonyl grouping has long been recognized among organic chemists, but little application has been made of this functional unit in synthetic operations.[1] We have recently demonstrated the advantages of this highly electrophilic system in the fusion of β-lactam nuclei to the five- and six-membered rings of carbacepham, carbapenam, and penam systems.[2a-c]

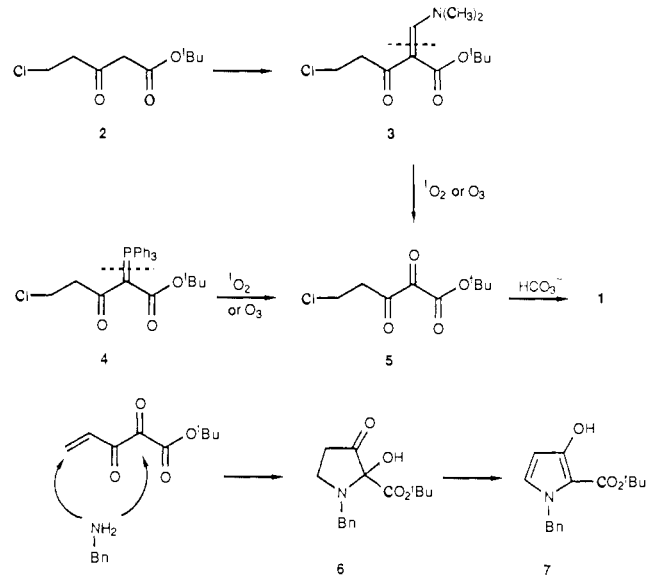
We now report methods for the formation of vinyl tricarbonyl systems of type **1** incorporating an aggregate of reactive electrophilic functional groups in a readily available, stable molecule. In its chemical behavior, this vinyl tricarbonyl system acts as a



1

di- or trielectrophile, permitting the facile formation of carbocyclic and heterocyclic systems of synthetic interest. Thus, a reagent such as a primary amine, having 2-fold nucleophilic capability, may undergo conjugate addition to the α,β-unsaturated assembly in **1** with concomitant attack at the highly reactive central carbonyl of the proximate tricarbonyl group. The resulting carbinolamines may form iminium ions which serve as sites for a third phase nucleophilic addition.

A starting material for the preparation of vinyl tricarbonyl **1** is *tert*-butyl-5-chloro-3-oxopentanoate **2**[4] which undergoes ready reaction with *N*,*N*-dimethylformamide dimethylacetal in methylene chloride to form the enamino derivative **3** (85%).[2] Treatment of the chloro enamine with singlet oxygen or ozone at −78 °C, followed by chromatography on silica gel and dehydrohalogenation with bicarbonate, yields vinyl tricarbonyl **1** (46%) as the monohydrate.



A more generally applicable procedure for the formation of this compound makes use of the chloro ylide **4** reported earlier by Cooke.[3,4] Ozone or singlet oxygen is passed through a solution of **4** and, after flash chromatography, the chloro tricarbonyl **5** is formed.[5] Dehydrohalogenation with saturated aqueous bicarbonate, followed by recrystallization from cyclohexane, yields vinyl tricarbonyl **1** as a white crystalline monohydrate, mp 66.5–67 °C (60% from the chloro ylide).[6] The fact that the central carbonyl group is hydrated was rigorously established by an X-ray crystallographic determination (Figure 1).[7]

The vinyl tricarbonyl reagent is stable in the form of a hydrate but reacts in the unhydrated form in solvents such as methylene chloride. An example of the use of **1** as a dielectrophile is provided in its reaction with benzylamine to form the hydroxy pyrrolidinone carboxylate **6** (93%).[8] Compound **6** can be readily converted by

(1) A review of the chemistry and reactions of vicinal polyketones including 1,2,3-vicinal tricarbonyls is given in the following: Rubin, M. B. *Chem. Rev.* **1975**, *75*, 177.

(2) (a) Wasserman, H. H.; Han, W. T. *Tetrahedron Lett.* **1984**, *25*, 3743. (b) Wasserman, H. H.; Han, W. T. *Tetrahedron Lett.* **1984**, *25*, 3747. (c) Wasserman, H. H.; Han, W. T. *J. Am. Chem. Soc.* **1985**, *107*, 1444.

(3) Cooke, M. P., Jr.; Burman, D. L. *J. Org. Chem.* **1982**, *47*, 4955.

(4) Ohta, S.; Shimbayashi, A.; Hatano, S.; Okamoto, M. *Synthesis* **1983**, 715.

(5) For related methods of preparing vicinal triketones by ozonolysis of ylide systems, see: (a) Schank, K.; Schuhknecht, C. *Chem. Ber.* **1982**, *115*, 2000, 3032. (b) Schank, K.; Lick, C. *Chem. Ber.* **1982**, *115*, 3890. (c) Schank, K.; Lick, C. *Synthesis* **1983**, 392.

(6) Spectral and analytical data: NMR (90 MHz, $CDCl_3$) 6.63 (d, 2 H, J = 6), 6.03 (t, 1 H, J = 6), 5.10 (br s, 2 H), 1.45 (s, 9 H); MS, EI, m/z (rel intensity) 185 (42), 167 (18.5), 139 (5.4), 57 (100); IR (CCl_4) 3500, 1750, 1720, 1700 cm^{-1}. Anal. Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.54; H, 6.98.

(7) Fractional coordinates, bond distances, torsional angles, and anisotropic temperature factors have been deposited at the Cambridge Crystallographic Data Centre.

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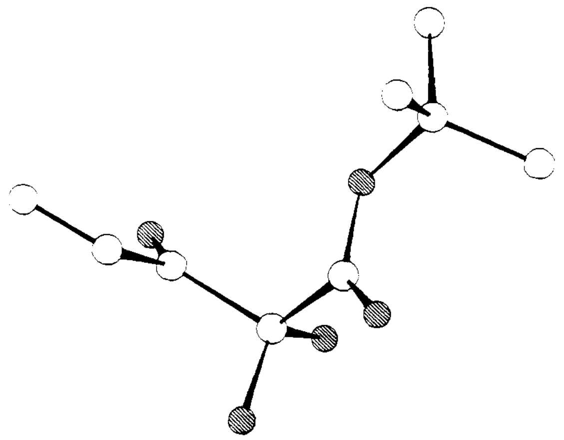
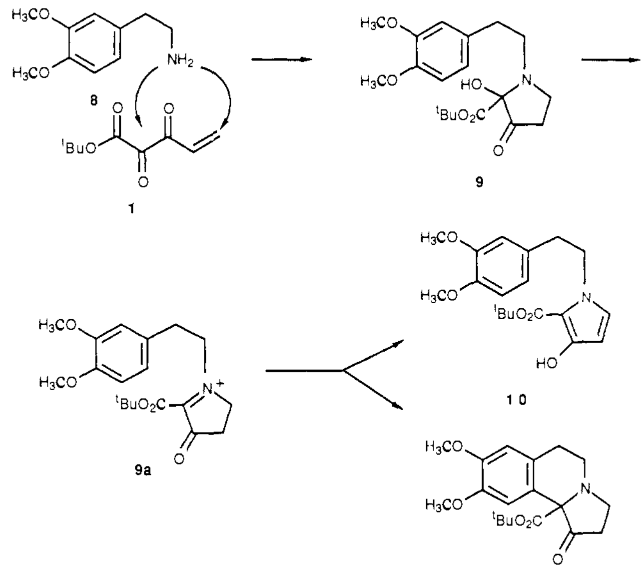


Figure 1. UPLOT drawing of the vinyl tricarbonyl hydrate **1**.

dehydrating agents such as silica gel to the corresponding 2-carbalkoxy-3-hydroxypyrrole **7** (77%).[9]

Reaction of **1** with reagents having multiple donor sites is illustrated in the two-step formation of the dihydroisoquinoline derivative **11** from dimethoxyphenylethyl amine **8**. The initially

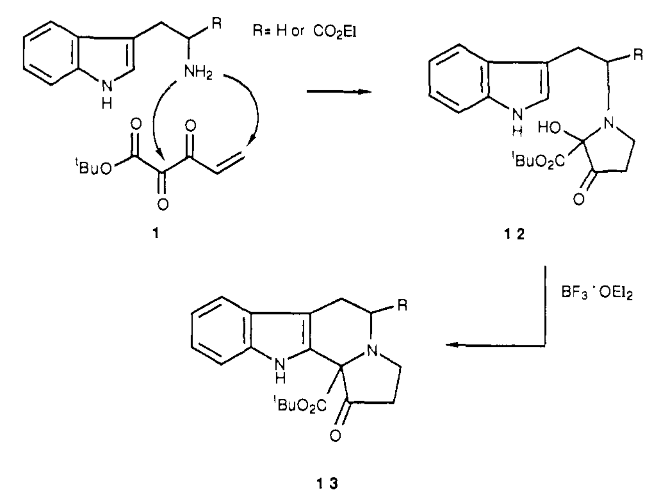


formed pyrrolidinone **9** can be converted on treatment with mild acid to the pyrrole derivative **10**. With $POCl_3$, however, cyclization of **9** takes place to form the tricyclic product **11** (41%), most probably through the iminium salt **9a**. We are investigating the conversion of **1** to **11** as the first step in the synthesis of alkaloids in the erythrina family.

A noteworthy example of the behavior of the vinyl tricarbonyl **1** as a trielectrophile is found in its reactions with tryptamine or tryptophan ethyl ester, leading to the formation of the tetracyclic system **13**. Here, carbinolamine **12** is formed initially by a double addition of the primary amine to the α,β-unsaturated ketone and the central carbonyl group. Treatment of **12** with $BF_3 \cdot Et_2O$ yields the tetracylic system **13**, in 73% yield from the vinyl tricarbonyl. In further reports, we will describe the use of this unusually reactive and versatile polyelectrophile in the formation of other systems, including indolizidines, tricyclic β-lactams, and cyclopentanones.

(8) To the vinyl tricarbonyl **1** (65 mg, 0.32 mmol) in 5 mL of CH_2Cl_2 was added benzylamine (34 mg, 0.32 mmol), and the reaction mixture was stirred at room temperature for 30 min. The solvent was removed in vacuo, and the oil was purified on a silica gel column (Et_2O/pentane, 1:3), yielding 90 mg (93%) of pyrrolidinone **6**: ^1H NMR (90 MHz, $CDCl_3$) 7.32 (m, 5 H), 4.23 (br s, 1 H), 3.83 (s, 2 H), 3.06 (t, 2 H, $J = 7$ Hz), 2.53 (t, 2 H, $J = 7$ Hz), 1.48 (s, 9 H); MS, CI, m/z (rel intensity) 291 (2.8), 217 (13.7), 191 (100).

(9) Momose, T.; Tanaka, T.; Yokota, T.; Nagamoto, N.; Yamada, K. *Chem. Pharm. Bull.* **1978**, *26*, 2224.



Acknowledgment. We are indebted to Dr. Gayle Shulte for providing the X-ray crystallographic data for the vinyl tricarbonyl. We also thank Robert Amici for his contributions in the synthesis of the dihydroisoquinoline system. This work was supported by NIH Grants GM 31350 and GM 07874.

Supplementary Material Available: ^1H NMR, IR, and MS data on compounds **6**, **7**, **11**, and **13** (3 pages). Ordering information is given on any current masthead page.

Characterization of a Novel μ_4-Peroxide Tetrairon Unit of Possible Relevance to Intermediates in Metal-Catalyzed Oxidations of Water to Dioxygen

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At some stage in the mechanism of oxygen evolution from water (eq 1), two oxygen atoms must approach one another to provide

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (1)$$

a stereochemical pathway for O–O bond formation. In Photosystem II,[1-3] this coupling is postulated to occur at a tetramanganese center,[4] for which several model complexes have been synthesized.[5] These models offer limited insight into the critical O–O bond forming step, however. Recently, we reported a compound, $[Fe_6O_2(OH)_2(O_2CPh)_{12}(H_2O)(1,4\text{-dioxane})]$ (**1**),[6] in which one could envision oxidative coupling of two closely positioned [2.46 (1) Å] hydroxide ligands mutually supported by four central iron atoms of a hexanuclear cluster. We now wish to describe the synthesis and properties of a novel μ_4-peroxide analogue, $[Fe_6(O)_2(O_2)(O_2CPh)_{12}(OH_2)_2]$ (**2**), prepared by simple ligand substitution of one peroxide for two bridging hydroxides (eq 2; the curved lines denote benzoate groups). Compound **2**

(1) Dismukes, G. C. In *Manganese in Metabolism and Enzyme Function*; Schramm, V. L., Welder, F. C., Eds.; Academic Press: 1986; pp 275–309.
(2) Babcock, G. T. In *New Comprehensive Biochemistry: Photosynthesis*; Amesz, J., Ed.; Elsevier: Amsterdam, 1987; pp 125–158.
(3) (a) Brudvig, G. W.; Crabtree, R. H. *Prog. Inorg. Chem.*, in press. (b) Brudvig, G. W. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; ACS Symposium Series No. 372; American Chemical Society: Washington, DC, 1988; p 221.
(4) Amesz, J. *Biochim. Biophys. Acta* **1983**, *726*, 1.
(5) (a) Brudvig, G. W.; Crabtree, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 4586. Christou, G.; Vincent, J. B. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; ACS Symposium Series No. 372; American Chemical Society: Washington: DC, 1988; p 239. (c) Dismukes, G. C. *Chimica Scripta* **1988**, *28A*, 99. (d) Bhula, R.; Gainsford, G. J.; Weatherburn, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 7550, and references cited therein.
(6) Micklitz, W.; Lippard, S. J. *Inorg. Chem.* **1988**, *27*, 3067.

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