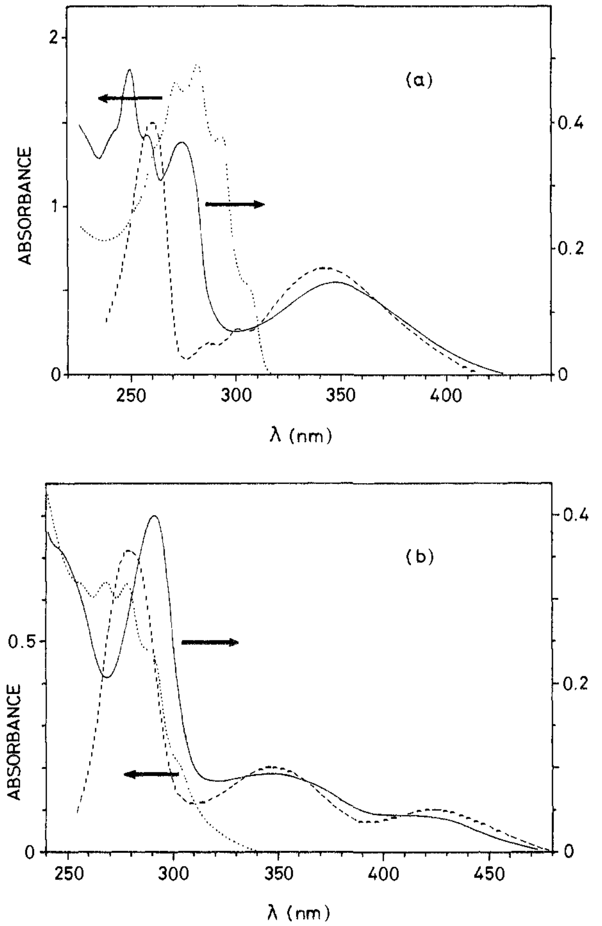
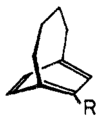


Figure 1. Electronic absorption spectra of 3 in EPA at 77 K prior to irradiation (dotted lines), transients generated upon irradiation of 3 with 254-nm light (solid lines),[10] and 6[1a,13] (dashed lines): (a) R = H; (b) R = CO_2CH_3. Small peaks at 285 and 300 nm in the spectrum of 6a are due to *p*-xylylene.[1a]



6

366-nm light, the developed absorption was efficiently bleached and the absorption spectrum of 3a was largely restored. This behavior was reminiscent of [4]paracyclophane (6)[1a] and suggested that the intermediate photochemically reverted to 3a. Irradiation of 3b in an EPA glass with 254-nm light at 77 K also led to a species which showed λ_{max} at 291, 345, and 415 (sh) nm in the UV-vis spectrum (Figure 1b)[10,12] and thermal and photochemical behavior similar to that observed above. In Figure 1 are also shown the absorption spectra of 6a and 6b which we recently reported.[1a] The striking similarity in shape of the presently observed spectra to those of the corresponding 6 in the long wavelength region (>265 nm)[13] indicates that the transient species produced here would certainly be **1**. In **1**, the π bond system in the four carbon bridge and that of the extremely bent benzene ring are nearly orthogonal to each other, and there could be little interaction between them.[14] If the species generated had the structure of **2**, the observed spectra would be much different from those of **6a** and **6b**. In **2**, the π bonds overlap each other only weakly, and such a poorly conjugated system tends to exhibit a broad, weak absorption spectrum.[15] Cyclooctatetraene is a notable example,[16] and the π bond system of **2** may be viewed as that of cyclooctatetraene perturbed by the etheno bridge double bond.

Thus, on the basis of the regioselective addition of cyclopentadiene to give **4** and **5** and the transient absorption spectra remarkably similar in shape to those of the corresponding **6**, it may be concluded that the irradiation of **3** leads to a species which is best represented by the structure **1**. This conclusion, however, does not rule out the possibility that the structure **2** represents a local minimum on the potential energy surface of bicyclo[4.2.2]decapentaene and may even be more stable than **1**, though the present photoreaction of **3** provided no evidence suggesting that such was the case. If **1** were less stable than **2**, **1** would be separated from **2** by a sizable energy barrier (>6 kcal/mol) since the absorption spectra of **1a** and **1b** showed no sign of decay within 1 h at 77 K.

Because a 1,3-butadienylene bridge is shorter and less flexible than a tetramethylene chain, the benzene ring in **1** will be more severely bent than that in **6**. Thus **1** will represent the most strained of the [*n*]paracyclophanes known so far.[1]

Supplementary Material Available: Spectroscopic data for **4a**, **4b**, **5a**, **5b**, and the secondary products (6 pages). Ordering information is given on any current masthead page.

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(12) Molar absorptivity at 291 nm was estimated to be ca. 9000.

(13) In the short wavelength region (<265 nm), **1** exhibited peaks which would be due to the diene chromophore in the bridge. Since molar absorptivity of **6** has not yet been determined, the absorption intensity of the spectrum of **6** was adjusted to that of **1** in Figure 1.

(14) When the π electron systems of formally conjugated chromophores are at right angles to each other and do not interact, the observed spectrum will appear to be a summation of the spectra of the separate chromophores.[15]

(15) Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; Wiley: New York, 1962; Chapter 15.

(16) (a) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Justus Liebigs Ann. Chem.* **1948**, *560*, 1. (b) Cope, A.; Bailey, W. J. *J. Am. Chem. Soc.* **1948**, *70*, 2305.

New Types of Metallacycles Formed by Cycloaddition of Imines and $Bu^tN{=}O$ with Mn and Re Carbyne Complexes

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Received August 15, 1988

Carbene complexes have found an impressive synthetic utility in organic chemistry through a variety of carbene transfer and cycloaddition reactions.[1] In contrast, carbyne complexes have far fewer applications, partly because their overall chemistry is significantly less developed.[2] For example, the only well-demonstrated cycloaddition reaction is with alkynes to form metallacyclobutadienes,[1,3] although transient metallacycles may form in reactions of metal carbynes with isocyanates,[4] nitriles,[5] ketones,[5] and aldehydes.[5] We have examined the cycloaddition behavior

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(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 16.

(2) Kim, H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51.

(3) (a) Churchill, M. R.; Ziller, J. W.; McCullough, L.; Pedersen, S. F.; Schrock, R. R. *Organometallics* **1983**, *2*, 1046. (b) Pederson, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808. (c) McCullough, L. G.; Listemann, M. L.; Schrock, R. R.; Churchill, M. R.; Ziller, J. W. *J. Am. Chem. Soc.* **1983**, *105*, 6729.

(4) Gill, D. S.; Baker, P. K.; Green, M.; Paddick, K. E.; Murray, M.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 986.

(5) Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1986**, *5*, 398.

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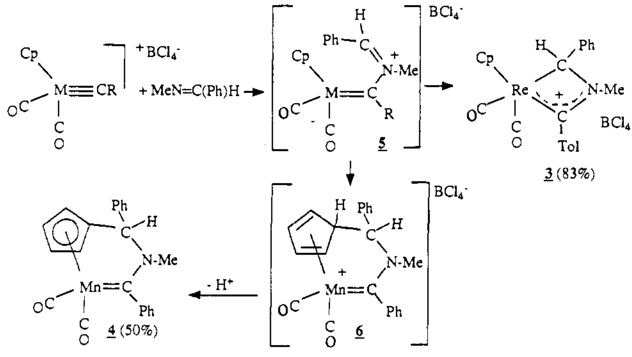
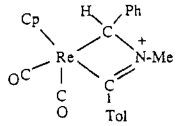
Scheme I

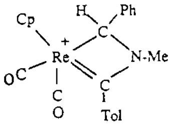


of the carbyne complexes $[\mathrm{Cp(CO)_2M{\equiv}CR}]^+$ (**1**, M = Re, **2**, M = Mn)[6] and report herein the formation of new types of metallacycles from the reactions of **1** and **2** with imines and Bu^{t}N=O.

As shown in Scheme I, which also illustrates the probable mechanism, complex **1** rapidly undergoes a net [2 + 2] cycloaddition of MeN=C(Ph)H (15 min, -20 °C) to form complex **3**, the first example of a metallaazetine.[7] Metallacycle **3** was isolated as a microcrystalline solid and has been spectroscopically[8] and crystallographically[9a,b] characterized, Figure 1. It forms as a 1:1 mixture of diastereomers, a consequence of the chiral nature of the rhenium center and the sp^3 ring carbon. The metallaazetine ring is planar, and the diastereomer shown in Figure 1 has the Cp ligand and the hydrogen substituent of the sp^3 ring carbon on the same side of the ring, an arrangement that is reversed in the other diastereomer. The metallaazetine ring is drawn in Scheme I as a hybrid of the two resonance forms A and B. The dominant importance of A is implied by the C(8)–N bond distance of 1.285 (8) Å which is a typical double bond value[10] and is significantly shorter than the C(9)–N distance of 1.468 (9) Å.

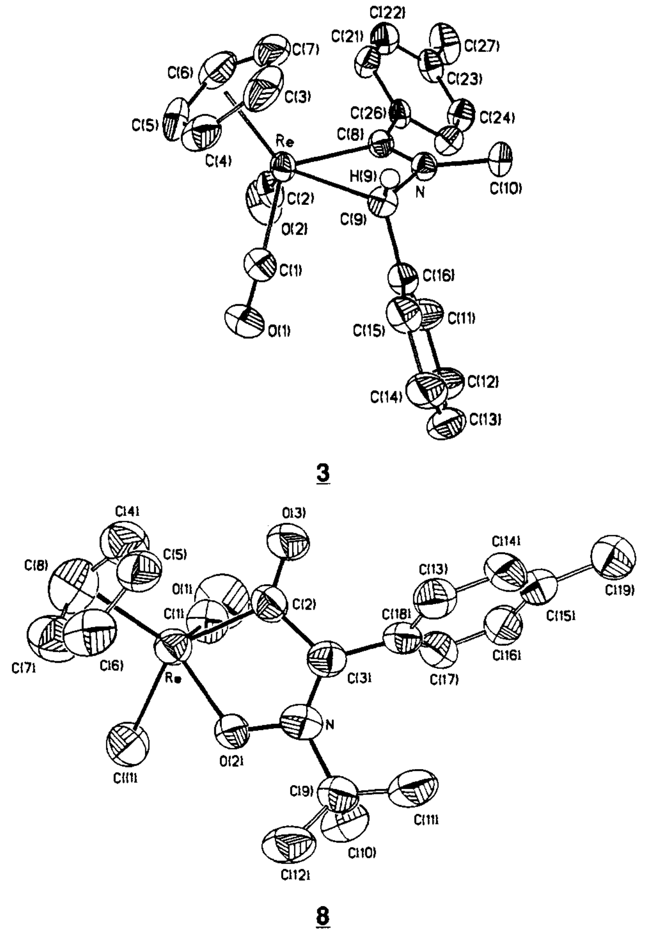


A



B

Surprisingly, the manganese carbyne complex **2** reacts with imine at -78 °C to insert the imine between the carbyne and a cyclopentadienyl ring carbon to give complex **4**, Scheme I. This species was isolated as a spectroscopically[11] characterized yellow solid which shows four equal intensity Cp ^{1}H NMR resonances and a carbene ^{13}C NMR resonance at δ 228. As illustrated in Scheme I, the initial step in both of the above reactions likely involves nucleophilic addition of the imine to the carbyne carbon since complexes **1** and **2** have been shown to readily add nucleophiles to this ligand.[2,12] Such reaction would generate the carbene complex **5** which could undergo ring closure to give the metallaazetine **3** or attack the Cp ring to form **6** which would yield **4** upon deprotonation.



3

8

Figure 1. ORTEP drawings of complexes **3** and **8**.

In an attempt to block the path leading to **4**, a similar reaction was conducted with the C_5Me_5 (Cp*) analogue of **2**, since it was reasoned that a methyl group would not likely be displaced from the Cp* ring. Surprisingly, this reaction follows the same course, and the product **7** results from electrophilic substitution of a Cp* methyl group by the imine carbon, eq 1. To our knowledge, this is the first example of such an electrophilic displacement reaction on a Cp* ring. Complex **7**[13] shows four equal intensity ^{1}H NMR resonances due to the inequivalent Cp* methyl groups and a ^{13}C NMR carbene resonance at δ 288.7.

Carbyne complex **1** also reacts with Bu^{t}N=O to form the first example of a metallaisoxazolone[7] (**8**), eq 2. A CO ligand has been incorporated into the metallacycle, and the vacancy left by the CO has been filled by a chloride, apparently abstracted from BCl_4^-. Complex **8** has been spectroscopically[14] and crystallographically characterized,[15] Figure 1. The metallacycle ring is

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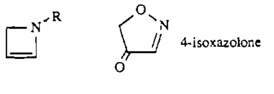
(6) Fischer, E. O.; Meineke, E. W.; Kreiβl, F. R. *Chem. Ber.* **1977**, *110*, 1140.

(7) The metallaazetine and the metallaisoxazolone nomenclature are derived from the organic rings sketched below:



(8) **3**: C, H Anal; ^{1}H NMR (acetone-d_6) δ 2.46 (s, 6 H, Tol-C*H*$_3$), 3.47 (s, 3 H, N-C*H*$_3$), 3.58 (s, 3 H, N-C*H*$_3$), 5.48 (s, 1 H, C*H*(Ph)), 5.61 (s, 1 H, C*H*(Ph)), 5.81 (s, 5 H, *Cp*), 6.45 (s, 5 H, *Cp*), 7.19–7.67 (m, 18 H, aryl); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 16.2, 20.1 (*C*H(Ph)), 21.6 (Tol-*C*H$_3$), 45.5, 46.6, (N-*C*H$_3$), 93.5, 95.3, (*Cp*), 124.7–144.0, (Ph, Tol), 197.3, 199.0 (*C*O), 200.2 (*C*-Tol), 201.2, 201.4, (*C*O); IR (CH_2Cl_2) ν_{CO} = 1975, 2042 cm^{-1}.

(9) **3**: triclinic, *P*1(bar), a = 10.367 (2) Å, b = 11.306 (2) Å, c = 11.858 (2) Å, α = 83.96 (2)°, β = 83.04 (2)°, γ = 67.78 (2)°, V = 1274.6 (5) Å^3, Z = 2. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms, except H(9) which was found and isotropically refined, were refined as idealized isotropic contributions. The phenyl ring was given rigid body constraints. $R(F)$ = 3.56%, $R(wF)$ = 4.53% for 3772 observed reflections at the $5\sigma(F_o)$ level. Re–C(8), 2.136 (4); Re–C(9), 2.250 (6); C(8)–N, 1.285 (8); C(9)–N, 1.468(9) Å. C(8)–Re–C(9), 60.1 (3); Re–C(8)–N, 102.3 (5); Re–C(9)–N, 91.4 (4); C(8)–N–C(9), 105.8 (5)°.

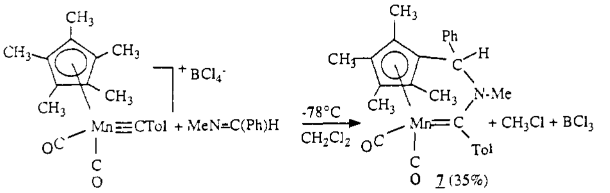
(10) Yoder, C. H.; Suydam, F. H.; Snavely, F. A. *Chemistry*, 2nd ed.; Harcourt Brace Jovanovich: New York, 1980; p 807.

(11) 4: C, H Anal; ^{1}H NMR ($CDCl_3$) δ 2.69 (s, N-C*H*$_3$), 4.25, 4.58, 4.77, 4.95 (s, 1 H, *Cp*), 5.63 (s, 1 H, C(*H*)Ph), 6.94–7.42 (m, Ph); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 40.1 (N-*C*H$_3$), 87.0, 83.0, 80.4, 78.0, 71.6 (*Cp*), 233.4, 233.4, (CO), 288.0 (*C*(Ph)R), 109.3–149.8 (Ph); IR (CH_2Cl_2) ν_{CO} = 1930, 1836 cm^{-1}. MS(EI), m/z = 383 (M$^+$).

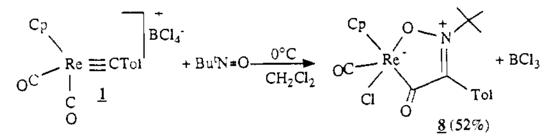
(12) (a) Fischer, E. O.; Jiabi, C.; Kurt, S. *J. Organomet. Chem.* **1983**, *253*, 231. (b) Fischer, E. O.; Wanner, J. K. R. *Chem. Ber.* **1985**, *118*, 2489.

(13) **7**: C, H Anal; ^{1}H NMR (CD_2Cl_2) δ 1.19, 1.63, 1.89, 2.14 (s, 3 H, Cp-C*H*$_3$), 2.28 (s, Tol-C*H*$_3$), 2.90 (s, N-C*H*$_3$), 6.07 (s, *Cp*), 6.8–7.5 (m, aryl); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 10.2, 10.9 (Cp-*C*H$_3$), 21.0 (Tol-*C*H$_3$), 40.1 (N-*C*H$_3$), 71.1 (*C*H(Ph)), 90.9, 93.1, 97.7, 101.2, 102.5 (*Cp*), 128.5–149.3 (Ph, Tol), 235.4, 235.5, (*C*O), 288.7 (*C*Tol); IR (CH_2Cl_2) ν_{CO} = 1913, 1848 cm^{-1}; MS(EI), m/z = 453 (M$^+$).

(14) **8**: C, H Anal; ^{1}H NMR (CD_2Cl_2) δ 1.45 (s, Bu^t), 2.40 (s, Tol-C*H*$_3$), 5.54 (s, *Cp*), 7.02–7.27 (m, Tol); ^{13}C{^{1}H}, NMR (CD_2Cl_2) δ 21.5 (Tol-*C*H$_3$), 30.0 (Bu^t-*C*H$_3$), 74.5 (*C*(CH$_3$)$_3$), 125.3, 129.2, 130.2, 140.9 (Tol-*C*), 160.7 (*C*-Tol), 204.1 (*C*O), 231.1 (ring *C*O); IR (CH_2Cl_2): ν_{CO} = 1930 cm^{-1}.



(1)



(2)

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.

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(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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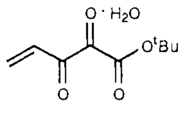
Received September 12, 1988

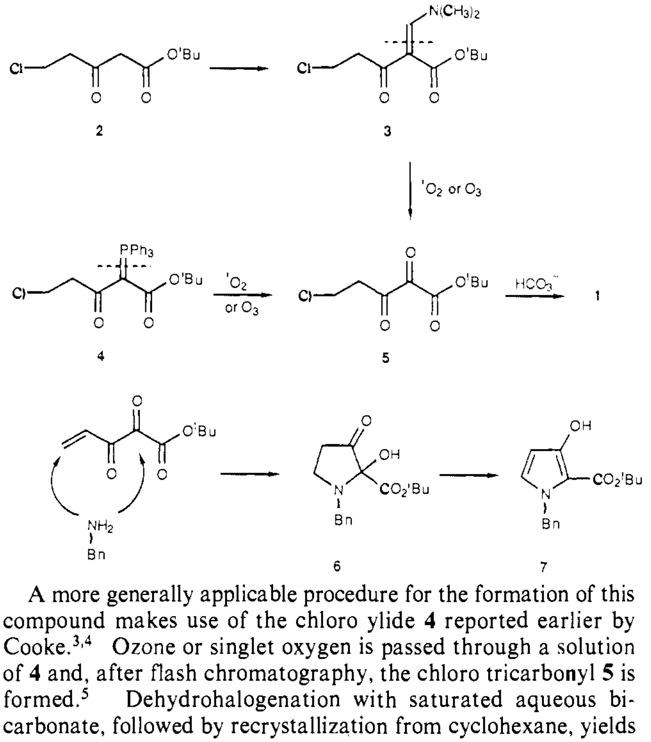
The greatly enhanced reactivity of the central carbonyl of a 1,2,3-tricarbonyl grouping has long been recognized among organic chemists, but little application has been made of this functional unit in synthetic operations.[1] We have recently demonstrated the advantages of this highly electrophilic system 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 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.



1

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

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(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.

0002-7863/89/1511-0371$01.50/0