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$$K_C = \frac{(\text{lactam, } \alpha \text{ anion})}{(\text{lactam}) \cdot (\text{anion})^{\alpha}} \text{ and } K_E = \frac{(\text{lactim, } \beta \text{ anion})}{(\text{lactim}) \cdot (\text{anion})^{\beta}}$$

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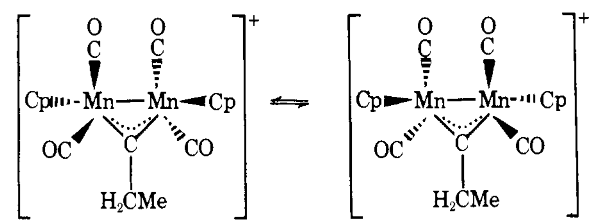
Nucleo- and Electrophilicity of $(C_5H_5)_2Mn_2(CO)_4(\mu\text{-}\eta^1\text{-}CCH_2)$. New Paths to Carbyne and Allene Ligands

Sir:

We have recently reported[1] the synthesis and structure of $Cp_2Mn_2(CO)_4(\mu\text{-}\eta^1\text{-}CCH_2)$, Ia, a rare example of a complex of the unsubstituted vinylidene ligand. This complex is unusual in that the carbon-carbon double bond of the vinylidene ligand does not donate directly to either metal atom. We report here the results of a study of the nucleophilic and electrophilic reactivity of this bond.[2]

Compound Ia offers a variety of sites for addition of H^+: the Mn—Mn bond, the carbonyl oxygen, the vinylidene C=C bond, and the magnanese-vinylidene σ bond. Addition of 4 equiv of CF_3CO_2H to compound Ia in CD_3CN results in complete conversion into violet $[HCp_2Mn_2(CO)_4CCH_2]$-O_2CCF_3, IIa, characterized by sharp ^1H NMR singlets at δ 5.27 (Cp, 10 H) and 4.45 (3 H); no hydride resonance is evident.[3] The ^1H NMR of a CD_3CN solution formed by addition of 1 equiv of CF_3CO_2H to Ia exhibits four broad resonances due to proton exchange of IIa with Ia.[4] To further confirm that the protonation site is the β carbon of the vinylidene bridge, we have examined an alternative substrate. The dimer $Cp_2Mn_2(CO)_4(\mu\text{-CCHMe})$,[5] Ib, exhibits inequivalent cyclopentadienyl rings up to 100 °C since the asymmetrically substituted vinylidene bridge does not participate in any facile dynamic process. Addition of 4 equiv of CF_3CO_2H to this dimer in CD_3CN forms IIb, characterized by a cyclopentadienyl *singlet* (δ 5.28) and an ABX_3 ethyl pattern (CHH′ at 4.84 and 4.36, with CH_3 at 1.61). The same behavior is observable in CD_2Cl_2 or CD_3NO_2. The diastereotopic character of the methylene protons in IIb indicates that the enantiomerization process shown in Scheme I is slow. Taken together, these results demonstrate a new synthesis of the μ-carbyne unit by β addition to a vinylidene bridge

Scheme I

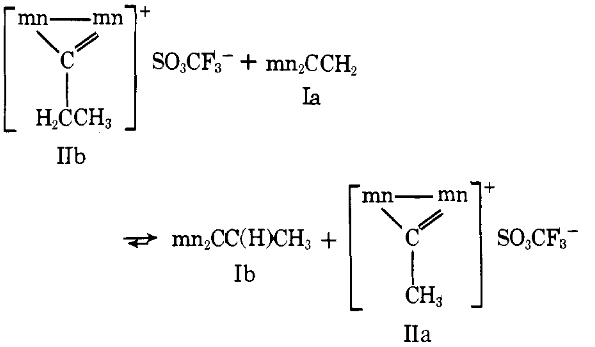


$$[\mathrm{CpMn(CO)_2}]_2(\mu\text{-CCHR}) + \mathrm{H}^+ \rightarrow [\mathrm{CpMn(CO)_2}]_2(\mu\text{-CCH_2R})^+ \tag{1}$$

This method contrasts with all previous carbyne syntheses, which involve *removal* of one or more groups from the α carbon.[6] The extension of this new procedure to the terminal vinylidene-terminal carbyne transformation (IV → V) merits further study as a step in the sequential conversion[2] of coordinated acetylide into carbyne (III → V), using electrophiles E^+.

$$\underset{\text{III}}{[\mathrm{M{-}C{\equiv}CR}]^{n+}} \xrightarrow{E^+} \underset{\text{IV}}{[\mathrm{M{=}C{=}C(E)R}]^{n+1}} \xrightarrow{E^+} \underset{\text{V}}{[\mathrm{M{\equiv}C{-}CE_2R}]^{n+2}} \tag{2}$$

The acidity of the β hydrogens in the cationic carbyne complexes IIa and IIIb, shown by their exchange with $CF_3CO_2^-$ and with I, allows a direct competition experiment (eq 3). Surprisingly, combination of equimolar Ia and IIb in CD_3NO_2 results in complete conversion into Ib and IIa; steric factors appear to control this equilibrium.



(3)

mn = $CpMn(CO)_2$

Complex Ia also reacts with strong nucleophiles. Treatment of Ia with $LiEt_3BH$ in THF,[7] followed by reaction with methyl iodide, yields two carbonyl compounds. Chromatography on Florisil (toluene eluant) brings down a green and then a maroon band (VI). The ^1H NMR spectrum of compound VI, $Cp_2Mn_2(CO)_3C_3H_4$,[8] establishes equivalent cyclopentadienyl rings, but two types of C_3H_4 protons in equal numbers. Remarkably, the IR spectrum of VI suggests the presence of a bridging carbonyl. The exact nature of compound VI, established by X-ray crystallography,[9] is evident in Figure 1. The molecule has approximate twofold rotational symmetry, being comprised of *trans*-CpMnCO groups bridged by both CO and allene. The allene fragment in VI is bent at an angle of 146.5°. This work is the first accurate structural definition of a sym-

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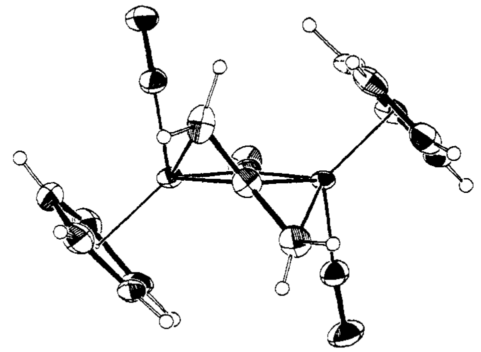
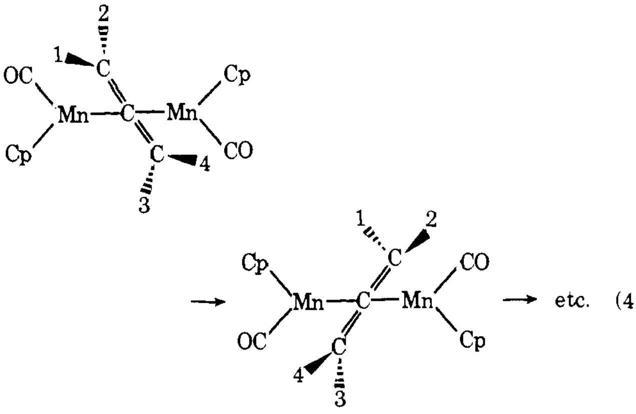


Figure 1. Molecular structure of $(C_5H_5)_2Mn_2(CO)_3(\mu\text{-}\eta^3\text{-}C_3H_4)$. Structural parameters: Mn-CO, 1.775 (5) (terminal); 1.972 (5) (bridge); Mn-CH_2, 2.173 (5); Mn-C (allene), 1.976 (5); C-C (allene), 1.393 (8); Mn-Mn, 2.691 (2) Å.

metrical carbonyl bridge between two manganese atoms. The AA′BB′ pattern evident[8] in the ^1H NMR spectrum of the allene bridge is due to protons proximal and distal with respect to the Mn—Mn bond. Compound VI, like $Cp_2Mo_2(CO)_4(\mu\text{-}\eta^3\text{-}C_3H_4)$,[10] is thus relatively rigid with respect to the fluxional process shown in eq 4 (μ-CO omitted), presumably because the plausible transition state involves major disruption of metal-allene bonding.



(4)

This report represents the first synthesis of an allene within the metal coordination sphere. Among synthetic routes to allenes, the formation of a carbon-carbon multiple bond in one step finds precedent only in the Wittig synthesis of allenes from $R_2C{=}C{=}PPh_3$ and OCR'_2. The source (i.e., CO or CH_3I) and ultimate location of the added carbon and hydrogen in VI are currently under investigation as essential preliminaries to any mechanistic proposal for this unusual transformation.

Acknowledgment. This work was supported by the National Science Foundation (CHE 77-10059) and the M. H. Wrubel Computing Center. Mass spectra were recorded at the Michigan State University Mass Spectrometry Facility and $CpMn(CO)_3$ was a gift from the Ethyl Corporation.

Supplementary Material Available: A list of atomic coordinates and thermal parameters for $(C_5H_5)_2Mn_2(CO)_3C_3H_4$ (1 page). Ordering information is given on any current masthead page.

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(3) Addition of HSO_3CF_3 to a benzene solution of I precipitates the corresponding fluorosulfonate salt. This compound, in THF, shows infrared bands at ν 1990 (s, br) and 1980 (sh) cm^{-1}.

(4) Treatment of Ia with excess CF_3CO_2D yields IIa-d_1 in which the intensity of the δ 4.45 resonance decreases over a period of 1 h owing to multiple deuteration. This establishes the time scale of proton transfer from IIa to $CF_3CO_2^-$.

(5) Synthesized from propyne and characterized by mass, (ν_{CO} 1978 (m), 1951 (s), 1925 (s)), and ^1H NMR spectroscopy (δ 4.69 (Cp), 4.64 (Cp), 7.02 (CH, q, $J = 7$ Hz), 2.27 (CH_3, d, $J = 7$ Hz), all in CD_2Cl_2).

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(8) The mass spectrum shows this parent ion as well as fragments formed by loss of CO and C_3H_4. IR (hexane): 1910 (s), 1760 cm^{-1}. ^1H NMR (C_6D_6): δ 3.70 (Cp, 10 H), 3.79 (=CH, 2 H, "triplet" with a 2-Hz spacing), 2.71 (=CH, 2 H, 2-Hz "triplet").

(9) Crystallographic data (−176 °C): $a = 13.253$ (5) Å, $b = 15.768$ (7) Å, $c = 7.376$ (3) Å, $\cos \beta = -0.4352$ (3) °, $V = 1387$ Å^3, $Z = 4$; in space group $P2_1/a$; $R(F) = 0.0547$, $R_w(F) = 0.0773$ for 2316 observed ($F_o^2 > \sigma(F_o^2)$) reflections using anisotropic thermal parameters for all nonhydrogen atoms; all hydrogen atoms were refined isotropically.

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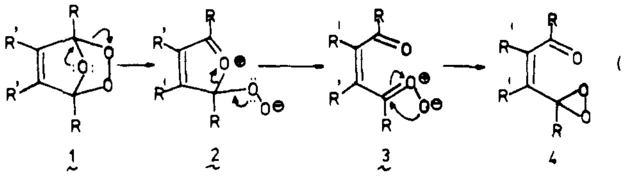
Oxygen Atom Transfer by Furan Endoperoxides[1]

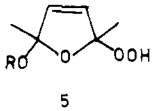
Sir:

A recent communication[2] that carbonyl oxides of nonozonolytic origin can epoxidize olefins prompts us to report our own observations that furan endoperoxides **1** are capable of oxidizing (a) tetramethylethylene to its epoxide, (b) diphenyl sulfide to its sulfoxide, and (c) adamantanone to its lactone. We suspected that the oxygen-atom-transferring species was either the unusual carbonyl oxide **3** or the novel dioxirane **4**, both thought to be derived from the dipolar species **2** by ring opening of the endoperoxide **1** (eq 1). A similar mechanism has been suggested for the singlet oxygenation of tetraphenylpyrrole.[3]



(1)

This attractive mechanistic hypothesis, if experimentally verifiable, would permit rationalization of a number of apparently isolated, but related, facts concerning the chemical behavior of furan endoperoxides. A few of these include the formation of (i) alkoxy hydroperoxides **5**[4] in alcoholic solvents, (ii) polymer **6**[5] in aprotic, polar solvents such as CH_3CN, (iii) 1,2-diacylethylenes **7**[5,6] on thermolysis in nonprotic, nonpolar solvents, (iv) epoxides **8**[7] and **9**[8] in the thermal decomposition, and (v) keto ester **10**[9] on heating of the corresponding furan endoperoxide. Thus, facts i and ii bespeak the interception of the dipolar species **2**, fact iii suggests that the "missing oxygen



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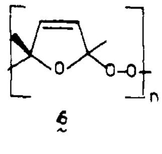

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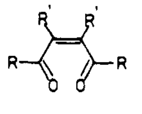

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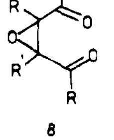

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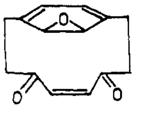

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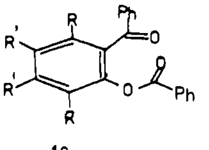

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