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Acetylene Isomerization by Manganese(I): Preparation and Structure of $(C_5H_5)_2Mn_2(CO)_4CCH_2$

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The multistep synthesis of $Cp_2Mn_2(CO)_4(\mu\text{-}CCH_2)$, from $CpMn(CO_2)(THF)$ and acetylene, is described. The crystal structure of the compound has been determined in order to firmly establish the formal 1,2-hydrogen migration and to evaluate the degree to which the hydrocarbon unsaturation does or does not interact with the metals. The complex crystallizes in space group $P2_1/c$ with $a = 8.788(3)$ Å, $b = 12.817(5)$ Å, $c = 13.974(6)$ Å, and $\beta = 112.17$ (3)°. Refinement of 2302 reflections collected at −130 °C led to a final R index of 0.075 and a final weighted R index of 0.090. Both hydrogen atoms of the bridging ligand were refined in order to establish the rotational conformation of this ligand. The CCH_2 ligand symmetrically bridges a Mn–Mn bond of length 2.759 (2) Å. The carbon–carbon bond length, 1.308 (10) Å, is typical of bond order 2, but there is an 11° twist of the CCH_2 ligand about the double bond.

Introduction

The $CpMn(CO)_2$ moiety supports a great variety of exotic addends. Cluster formation by this unit is a rather rare occurrence, however,[1] as is the formation of multiple bonds between manganese atoms.[2] We report here the product of a sequence of reactions which follow on mixing of $CpMn(CO)_2(THF)$ and HCCH in the presence of OH^-. The net result of these reactions is the isomerization of acetylene to the fragment CCH_2 which then bridges two $CpMn(CO)_2$ units. This work represents the first structural characterization of an unsubstituted "vinylidene" ligand. The appropriateness of this nomenclature is discussed in the light of our structural results and the recent characterization of "free" vinylidene.[3,4] Related acetylene isomerizations have been reported;[5-7] while this paper was in preparation, the first complex of a terminal vinylidene (CCH_2) was prepared.[8] A brief review of vinylidene complexes is available.[4]

Experimental Section

Synthesis of $Cp_2Mn_2(CO)_4CCH_2$. $CpMn(CO)_3$ (2.3 g, 0.011 mol) was dissolved in 60 mL of THF. The solution was placed in a toroidal reactor (Pyrex) which completely surrounds the emitting zone of a 550-W medium-pressure mercury lamp. The reactor is fitted with a septum through which gases can be bubbled by use of a syringe needle. The outlet of the reactor was connected to a Nujol bubbler.

The above solution was photolyzed at 10 °C for 1 h with an N_2 purge and for 1 h with a C_2H_2 purge. The C_2H_2 was bubbled first through a saturated aqueous sodium bisulfite solution in order to remove traces of acetone present in commercial acetylene. The lamp was turned off after 2 h and C_2H_2 was bubbled through the solution for an additional 3 h.

The resultant orange solution was filtered into a three-necked flask fitted with a reflux condenser. Aqueous KOH (1 mL of an 0.18 M solution) was added to the THF solution. The THF solution was refluxed under N_2 for 24 h, during which time the solution becomes purple.

After cooling to room temperature, the solution was filtered and pumped to dryness. A minimum of hexane was added and the hexane-soluble fraction was chromatographed on a silica column (30 cm × 4 cm). A yellow band eluted first; it was identified as $CpMn(CO)_3$ (0.72 g). Hexane moves a dark red band more slowly. The dark red solid obtained after removal of solvent from this band was identified as $Cp_2Mn_2(CO)_4CCH_2$ (IR in hexane 1975 (w), 1950 (s), 1921 (s) cm^{-1}; ^1H NMR in C_6D_6 τ 3.23 (2 H), 5.90 (10 H); mass spectrum, parent ion at m/e 378 followed by parent − N(CO), N = 3, 2, 0; $Cp_2Mn_2^+$ is also seen). Bands attributed to $\nu(C{=}C)$ and $\nu(CH_2)$ are observed at 1542 (s) and 1095 (m) cm^{-1} (in KBr).

Crystals suitable for the structural study were grown by dissolving $Cp_2Mn_2(CO)_4CCH_4$ in a minimum of pentane and allowing the pentane to slowly evaporate at −20 °C.

Trapping Experiments. (1) Excess cyclohexene (C_6H_{10}) and $Cp_2Mn_2(CO)_4CCH_2$ were combined in a minimum of C_6D_6. Heating the mixture (70 °C, closed NMR tube, 11 h) gave no detectable reaction (NMR). Photolysis (15 min) of this solution produced some precipitate. The IR of the remaining C_6D_6 solution revealed $Cp_2Mn_2(CO)_4CCH_2$, $CpMn(CO)_3$, $CpMn(CO)_2(C_6H_{10})$ (1945, 1885 cm^{-1} in C_6D_6; 1955, 1890 in hexanes), $CpMn(CO)_2CCH_2$ (1990 cm^{-1}), and an unidentified peak at 1980 cm^{-1}. Identification of $CpMn(CO)_2CCH_2$ and $CpMn(CO)_2(C_6H_{10})$ was by comparison to authentic samples prepared independently. The NMR of the product mixture confirmed the above. The ^1H NMR spectrum of $CpMn(CO)_2(C_6H_{10})$ is as follows: τ 6.25 (10 H, C_5H_5), 5.34 (2 H, HC=), 8.67 (8 H, CH_2), all in C_6D_6. The trapped vinylidene (7-methylenenorcarane) was not observed (^1H NMR detection).

Table I. Crystal Data for $(C_5H_5)_2Mn_2(CO)_4(CCH_2)$

molecular formula	$C_{16}H_{12}O_4Mn_2$
color of crystal	dark reddish brown
space group	$P2_1/c$
cell dimens (at −130 °C; 19 reflections)	
a, Å	8.788 (3)
b, Å	12.817 (5)
c, Å	13.974 (6)
β, deg	112.17 (3)
molecules/cell	4
cell vol, Å^3	1457.57
calcd dens, g/cm^3	1.723
radiation wavelength, Å	0.710 69
mol wt	378.14
linear absn coeff, cm^{-1}	16.777
cryst dimens, mm	0.036 × 0.126 × 0.11

(2) There is no thermal reaction between $Cp_2Mn_2(CO)_4CCH_2$ and norbornylene (C_7H_{10}) in C_6D_6. Photolysis of this solution produces $CpMn(CO)_3$, $CpMn(CO)_2(C_7H_{10})$ (ν_{CO} 1950, 1891 cm^{-1} in C_6D_6; ^1H NMR τ 5.93 (10 H), bound olefin obscured by free olefin), $CpMn(CO)_2CCH_2$, and an unidentified peak at 1978 cm^{-1}.

Structural Study. Unit cell dimensions and other crystal data are provided in Table I. Intensity data were collected at −130 °C. A total of 3058 reflections (including standards and space group extinctions) were collected in the range 4° ≤ 2θ ≤ 50°. The three standard reflections (020, 200, and 002) were measured after each 100 reflections. The data were processed in the usual manner,[9] using a value of the "uncertainty" factor in the determination of $\sigma(I)$ of 0.07. After averaging, a total of 2498 unique data were obtained. Absorption corrections were computed but not applied (max = 0.875, min = 0.673).

The structure was determined by using direct methods (LSAM). The resulting E map revealed the two Mn atoms as well as additional C and O atoms and spurious peaks. A Patterson map was computed to confirm the heavy-atom positions. A Fourier map phased on the two Mn atoms revealed the remaining atoms in the structure. Isotropic refinement followed by anisotropic refinement yielded a residual of 0.13. A difference map clearly indicated the positions of the two vinylidene hydrogen atoms, but the ten hydrogen atoms on the cyclopentadienyl rings were less well defined. Least-squares refinement using anisotropic thermal parameters on all nonhydrogen atoms and varying positional and isotropic thermal parameters on 12 hydrogen atoms resulted in final residuals of $R = 0.075$ and $R_w = 0.090$. The

Table II. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for $Cp_2Mn_2(CO)_4(CCH_2)$

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mn(1)	9277 (1)	3092 (1)	2998 (1)	16
Mn(2)	5939 (1)	3293 (1)	2500 (1)	14
C(1)	8452 (8)	1988 (6)	2165 (6)	23
C(2)	9522 (8)	3776 (7)	1946 (6)	27
C(3)	6402 (8)	2143 (5)	3314 (6)	20
C(4)	5804 (8)	4000 (5)	3552 (6)	18
C(5)	7776 (7)	4288 (5)	2830 (5)	18
C(6)	7925 (9)	5304 (6)	2904 (6)	26
C(11)	9965 (9)	3007 (7)	4654 (5)	29
C(12)	10398 (10)	2069 (6)	4304 (6)	31
C(13)	11530 (10)	2314 (8)	3842 (6)	36
C(14)	11810 (9)	3382 (8)	3924 (6)	34
C(15)	10858 (9)	3808 (6)	4420 (6)	32
C(21)	5330 (8)	3134 (6)	866 (5)	23
C(22)	4812 (8)	4119 (6)	1058 (5)	23
C(23)	3667 (8)	3963 (6)	1506 (6)	22
C(24)	3449 (8)	2872 (6)	1605 (5)	22
C(25)	4502 (8)	2352 (6)	1203 (5)	24
O(1)	8005 (6)	1263 (5)	1643 (5)	38
O(2)	9675 (7)	4216 (5)	1281 (5)	37
O(3)	6597 (6)	1450 (4)	3849 (4)	27
O(4)	5696 (7)	4436 (5)	4249 (5)	34
H(1)	7020 (113)	5695 (72)	2885 (68)	39 (21)
H(2)	9049 (91)	5710 (62)	2956 (57)	21 (15)

Table III. Bond Distances (Å) in $Cp_2Mn_2(CO)_4(CCH_2)$

Mn(1)-Mn(2)	2.759 (2)		
C(5)-C(6)	1.308 (10)		
C(6)-H(1)	0.93 (9)		
C(6)-H(2)	1.09 (8)		
Mn(1)-C(1)	1.801 (7)	Mn(2)-C(3)	1.811 (7)
Mn(1)-C(2)	1.794 (9)	Mn(2)-C(4)	1.769 (7)
Mn(1)-C(5)	1.979 (7)	Mn(2)-C(5)	1.971 (6)
Mn(1)-C(11)	2.163 (7)	Mn(2)-C(21)	2.149 (7)
Mn(1)-C(12)	2.159 (8)	Mn(2)-C(22)	2.158 (7)
Mn(1)-C(13)	2.131 (8)	Mn(2)-C(23)	2.135 (6)
Mn(1)-C(14)	2.143 (8)	Mn(2)-C(24)	2.140 (7)
Mn(1)-C(15)	2.154 (8)	Mn(2)-C(25)	2.146 (7)
O(1)-C(1)	1.154 (9)	O(3)-C(3)	1.132 (9)
O(2)-C(2)	1.137 (10)	O(4)-C(4)	1.158 (9)
C(11)-C(12)	1.404 (11)	C(21)-C(22)	1.402 (11)
C(11)-C(15)	1.403 (12)	C(21)-C(25)	1.419 (11)
C(12)-C(13)	1.410 (13)	C(22)-C(23)	1.386 (10)
C(13)-C(14)	1.388 (13)	C(23)-C(24)	1.425 (10)
C(14)-C(15)	1.385 (13)	C(24)-C(25)	1.417 (10)
Mn(1)-C(3)	2.983 (7)	Mn(2)-C(1)	2.945 (7)

Table IV. Bond Angles (Deg) in $Cp_2Mn_2(CO)_4(CCH_2)$

Mn(2)-Mn(1)-C(1)	77.3 (2)	Mn(1)-Mn(2)-C(3)	78.5 (2)
Mn(2)-Mn(1)-C(2)	101.1 (2)	Mn(1)-Mn(2)-C(4)	103.7 (2)
Mn(2)-Mn(1)-C(5)	45.6 (2)	Mn(1)-Mn(2)-C(5)	45.8 (2)
C(1)-Mn(1)-C(2)	89.9 (3)	C(3)-Mn(2)-C(4)	88.0 (3)
C(1)-Mn(1)-C(5)	116.4 (3)	C(3)-Mn(2)-C(5)	114.2 (3)
C(2)-Mn(1)-C(5)	78.8 (3)	C(4)-Mn(2)-C(5)	77.3 (3)
Mn(1)-C(1)-O(1)	176.5 (6)	Mn(2)-C(3)-O(3)	174.5 (6)
Mn(1)-C(2)-O(2)	179.5 (7)	Mn(2)-C(4)-O(4)	177.9 (6)
C(12)-C(11)-C(15)	107.2 (7)	C(22)-C(21)-C(25)	109.1 (6)
C(11)-C(12)-C(13)	107.5 (7)	C(21)-C(22)-C(23)	107.5 (6)
C(12)-C(13)-C(14)	108.4 (7)	C(22)-C(23)-C(24)	109.4 (6)
C(13)-C(14)-C(15)	107.9 (7)	C(23)-C(24)-C(25)	106.9 (6)
C(11)-C(15)-C(14)	109.0 (7)	C(21)-C(25)-C(24)	107.0 (6)
M(1)[a]-Mn-(1)-C(2)	123.2	M(2)-Mn(2)-C(4)	123.1
M(1)-Mn(1)-C(1)	120.2	M(2)-Mn(2)-C(3)	121.4
M(1)-Mn(1)-C(5)	118.0	M(2)-Mn(2)-C(5)	120.1
M(1)-Mn(1)-Mn(2)	130.2	M(2)-Mn(2)-Mn(1)	127.7
Mn(1)-C(5)-Mn(2)	88.6 (3)		
Mn(2)-C(5)-C(6)	135.4 (5)	Mn(1)-C(5)-C(6)	136.0 (5)
C(5)-C(6)-H(1)	118 (6)		
C(5)-C(6)-H(2)	123 (4)		
H(1)-C(6)-H(2)	119 (7)		

[a] M(*i*) denotes the midpoint of the Cp plane containing carbon atoms C(*iN*).

Table V. Distances from Least-Squares Planes and Dihedral Angles in $Cp_2Mn_2(CO)_4(CCH_2)$

plane no.	atoms defining plane	atom	dist of atom from plane, Å
1	C(11), C(12), C(13), C(14), C(15)	Mn(1)	−1.791
2	C(21), C(22), C(23), C(24), C(25)	Mn(2)	1.779
3	Mn(1), Mn(2), C(5), C(6)	H(1)	0.14
		H(2)	−0.19
4	Mn(1), C(1), C(2)	O(1)	0.071
		O(2)	−0.006
5	Mn(2), C(3), C(4)	O(3)	−0.071
		O(4)	−0.023
6	C(5), C(6), H(1), H(2)	Mn(1)	0.242
		Mn(2)	−0.279

plane no.	dihedral angles, deg	plane no.	dihedral angles, deg
1,2	8.3	3,6	10.9
1,3	40.9	1,4	47.2
2,3	39.0	2,5	47.2

Table VI. Angles between Lines and Planes

line no.	defining points	line no.	defining points
1	Mn(1), M(1)	3	H(1), H(2)
2	Mn(2), M(2)	4	Mn(1), Mn(2)

elements	angle, deg	elements	angle, deg
Cp(1),[a] line 1	89.2	line 1, line 4	49.8
Cp(2),[a] line 2	89.3	line 2, line 4	52.3
Cp(1), line 4	40.9	line 3, line 4	12.1
Cp(2), line 4	38.3		

[a] Cp(*i*) indicates the *i*th least-squares plane from Table V.

Table VII. Torsional Angles

atoms	angle, deg
Mn(1), C(5), C(6), H(1)	−170.4
Mn(2), C(5), C(6), H(2)	−167.9
Mn(1), C(5), C(6), H(2)	12.0
Mn(2), C(5), C(6), H(1)	9.7

Table VIII. Nonbonded Intramolecular Contacts (Å)

involving the vinylidene group		involving C(2), O(2), C(4), O(4)		involving C(1), O(1), C(3), O(3)	
C(4)-C(5)	2.340	C(4)-H(1)	2.735	C(1)-H(8)	2.741
C(2)-C(5)	2.397	C(4)-C(23)	2.765	O(3)-H(4)	2.798
C(22)-C(5)	2.845	C(2)-C(14)	2.782	C(3)-C(25)	2.806
C(15)-C(5)	2.848	C(2)-H(6)	2.829	O(1)-H(12)	2.822
H(9)-C(5)	2.848	C(4)-H(10)	2.833	C(1)-C(12)	2.830
H(7)-C(5)	2.883	C(4)-C(6)	2.892	C(1)-C(3)	2.836
C(4)-C(6)	2.892			O(1)-H(8)	2.862
H(7)-C(6)	2.913			C(1)-C(13)	2.863
H(9)-C(6)	2.991			C(3)-H(12)	2.889
H(2)-H(7)	2.690			C(3)-C(24)	2.938
H(1)-C(4)	2.735			C(3)-H(3)	2.944
H(1)-H(9)	2.871			C(1)-H(4)	2.954
H(2)-C(2)	2.959				

“goodness of fit” was 2.65 for 2302 reflections ($F > \sigma(F)$) and 248 variables. Final isotropic thermal parameters for the ten hydrogen atoms on the cyclopentadienyl rings ranged from 0.0 to 8.9, and it was decided to carry out final refinements with these atoms in calculated positions. By use of this model, final residuals for 2302 reflections are $R(F) = 0.075$ and $R_w(F) = 0.091$. The “goodness of fit” in the final cycle of refinement was 2.67, and the largest shift/standard deviation was 0.09. The ratio of observations to variables was 2302/208 = 11. An isotropic extinction correction parameter was included in the refinement; the maximum extinction correction was 33%. Refined fractional coordinates and equivalent isotropic thermal parameters appear in Table II. Anisotropic B's are available (see Supplementary Material). Bond lengths and angles are displayed in Tables III and IV so as to allow comparison of the two ends of the molecule. Least-squares planes and associated angles appear in Tables V–VII while selected nonbonded intramolecular

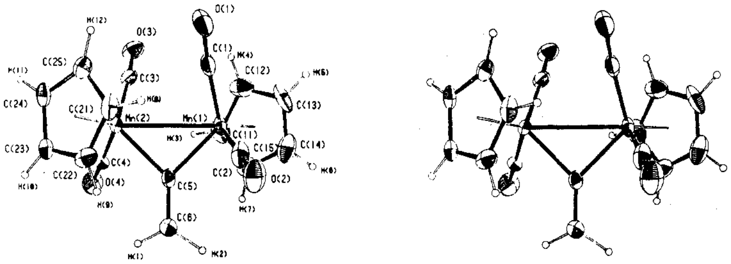


Figure 1. Stereoscopic view of $Cp_2Mn_2(CO)_4(CCH_2)$ perpendicular to the Mn(1), Mn(2), C(5) plane. Hydrogen atom temperature factors have been reduced for clarity.

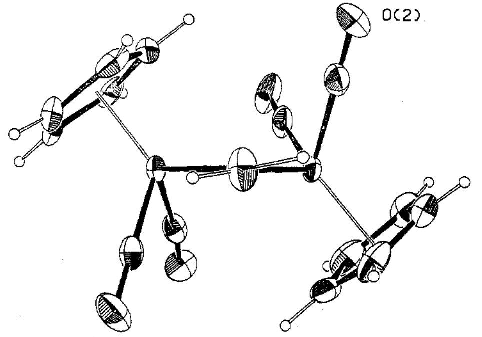


Figure 2. Molecular structure viewed along the line of the vinylidene double bond (C(5)–C(6)).

contacts are shown in Table VIII. All intermolecular contacts less than 3 Å involve hydrogen as one of the participants. The shortest of these (two H···H contacts at 2.4 Å) involve H(1) and H(2). Ring carbons deviate by less than 0.006 Å from their least-squares planes. Deviations from the best plane through C(5), C(6), H(1), H(2) are less than 0.010 Å.

Results and Discussion

Synthesis. The synthesis of $Cp_2Mn_2(CO)_4CCH_2$ reported here proceeds through the intermediates $CpMn(CO)_2(THF)$, $CpMn(CO)_2(\eta^2\text{-}HC_2H)$, an acetylene complex, and $CpMn(CO)_2CCH_2$, a "vinylidene" complex isoelectronic with the recently reported[8] $CpFeL_2(CCH_2)^+$ cations. A mechanistic study is in progress.

Several examples of substituted vinylidenes bound to metals are known,[5-8] but this work represents the first structural characterization of the parent hydrocarbon. Various calculations[4] place free vinylidene, :C=CH$_2$, some 38–46 kcal/mol above acetylene.

Description of the Structure. $Cp_2Mn_2(CO)_4CCH_2$ has the structure shown in Figures 1, 2, and 3. These, as well as end-to-end comparison of the distances and angles in Tables III–VI, confirm the noncrystallographic twofold rotational symmetry of the dimer. Deviations of the actual structure from such idealized symmetry were assayed quantitatively by using a program which determines a least-squares fit of the actual structure to the idealized symmetric model. The largest deviation occurs at C(6) (0.31 Å); other atoms deviate by 0.08–0.23 Å. The cyclopentadienyl carbon atoms deviate by less than 1σ from their respective planes. These two planes are nearly parallel (dihedral angle 8.3°), which follows from their nearly perfect trans stereochemistry and twofold rotational symmetry. The torsional angle M(1)–Mn(1)–Mn(2)–M(2) is 170.6°. Each ring midpoint makes approximately equal angles to two carbonyls, the vinylidene carbon and the second metal (Table IV).

The rotational conformation about the metal–metal bond is not the staggered form found in $[CpCr(CO)_3]_2$[10] due to the constraint imposed by the bridging ligand in $Cp_2Mn_2(CO)_4CCH_2$. In the resultant conformation (Figure 3), the torsional angle C(2)–Mn(1)–Mn(2)–C(4) is large (118.3°), forming a crevice which is occupied by the vinylidene group.

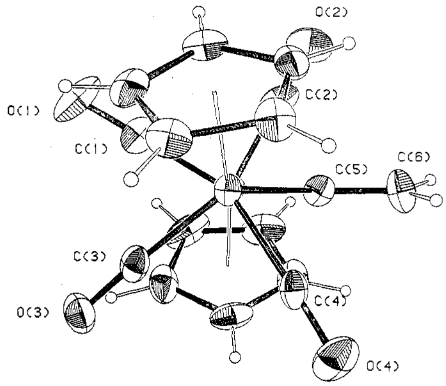


Figure 3. Rotational conformation, as viewed down the line Mn(1)–Mn(2).

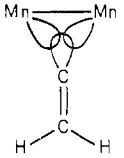
Crowding on the vinylidene side of the metal–metal bond (Figure 3) produces a small C(3)–Mn(2)–Mn(1)–C(1) torsional angle (69.4°) and acute angles Mn(1)–Mn(2)–C(4) and Mn(2)–Mn(1)–C(2). This leads to two short contacts (Mn(1)–C(3) and Mn(2)–C(1)) and a consequent bending (3° in excess of the angles at C(2) and C(4)) of the affected ligands. This bending is apparently due to nonbonded contacts with the opposite end of the molecule. As shown in Table VIII, these are more numerous for the odd-numbered carbonyls, and a significant fraction of these involve end-to-end C···H contacts. These repulsions are also evidenced by a statistically significant asymmetry in Mn–cyclopentadienyl carbon bond lengths. Ring carbons, 11, 12, 15, 21, 22, and 25, which are directed toward the metal–metal bond (and toward the odd-numbered carbonyls) show the longest distances to the metal.[11] Given such clear evidence for intramolecular crowding, there is no reason to attribute the observed Mn(1)–C(3) and Mn(2)–C(1) distances of less than 3 Å to a bonding interaction. The overall molecular structure of $Cp_2Mn_2(CO)_4CCH_2$ closely resembles those of $Cp_2Mn_2(CO)_4CCHPh$,[12] $Cp_2Re_2(CO)_4(\mu\text{-}CO)$,[13] and $Cp_2Mn_2(CO)_4(SEt)^+$,[14] with the exception of the longer metal–metal bonds (2.957 and 2.930 Å) in the latter two compounds.

The molecule contains a metal–metal bond bridged by an unsubstituted vinylidene (CCH_2) group. The ^1H NMR chemical shift of the CCH_2 protons is entirely consistent with an olefinic environment. The bridge is symmetric, both metal atoms being equidistant ($\Delta/\sigma < 1$) from C(5). The multiple bond within the vinylidene ligand is slightly shorter than the corresponding bonds in dimers bridged by CCHPh (1.35 (2) Å),[12] $CCPh_2$ (1.33 (1) Å),[15] and $CC(CN)_2$ (1.38 (3) Å).[16] The atoms Mn(1), Mn(2), C(5), and C(6) are coplanar. As shown in Table V, the vinylidene hydrogen atoms are displaced to opposite sides of this plane (see also Figure 2). Although the linear placement of terminal hydrogen atoms along the true bond vector is subject to significant systematic error, the angular location may be more accurately extracted from X-ray data. In the present case, the angle included between these bonds (119°) is reasonable, and the angles flanking the C-

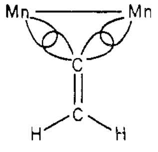
(5)–C(6) multiple bond are equal ($\Delta/\sigma < 1$). Having established the reliability of the angular placement of the vinylidene hydrogens, it becomes noteworthy that there exists an 11° twist about the vinylidene double bond (Table V, planes 3 and 6, and Figure 2). The internal consistency of this conclusion is also supported by the torsional angles in Table VII and the angle between lines 3 and 4 in Table VI. This twist is consistent with the C_2 molecular symmetry.

There is no evidence to indicate that the length of C=C bonds which are torsionally strained or those which undergo angular compression at one carbon (e.g., methylenecyclopropane) suffer significant ($\Delta/\sigma > 3$) bond length alteration.[17] Our results for $Cp_2Mn_2(CO)_4CCH_2$ conform to this notion. Although the twisting deformation in $Cp_2Mn_2(CO)_4CCH_2$ occurs so as to relieve potential nonbonded repulsions with ring atoms H(7) and H(9) (see Table VIII), it is sterically unfavorable in that it shortens the distances to C(2) and C(4). Consequently, this twist, which has been seen in other vinylidene bridges with more bulky groups,[15,16] cannot be clearly attributed to steric congestion. In fact, it is likely that this distortion yields a more suitable overlap of the two orbitals on C(5) with the metal orbitals.

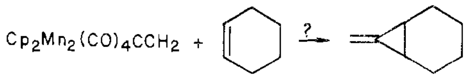
Consideration of the twist of the vinylidene moiety leads to the question of whether the μ-CCH_2 ligand in $Cp_2Mn_2(CO)_4CCH_2$ has carbene character (I) or is best represented as a geminally disubstituted olefin (II). We propose two criteria, each of which favors II. The Mn–C(5) distances in $Cp_2Mn_2(CO)_4CCH_2$ are only 0.045 Å shorter than those to the bridging CH_2 group in $(CH_3C_5H_4)_2Mn_2(CO)_4CH_2$;[18] this difference corresponds well with the smaller single bond radius of sp^2 than of sp^3 carbon (0.03 Å) and is thus consistent with a similar bonding mode in both compounds. Moreover, $Cp_2Mn_2(CO)_4CCHR$ (R = Me, Ph) are stereochemically rigid.[5,19] The two cyclopentadienyl rings in each of these dimers appear inequivalent by proton NMR at 25 °C due to the asymmetric substitution pattern on the vinylidene; thus, rotation of this bridging group about the C=C bond, if it occurs at all, is a significantly hindered process. This is consistent with structure II but is not readily accommodated by I. While these results provide some support for the importance of valence structure II, the ultimate resolution of this question is best left to reactivity studies now in progress. For example, we have probed $Cp_2Mn_2(CO)_4CCH_2$ for carbene (I) reactivity by attempting a transfer to cyclohexene (eq 1). The reaction was carried out with excess cyclohexene in order to stabilize the emerging $CpMn(CO)_2$ fragment and prevent secondary reaction promoted by manganese metal. While no reaction occurs at 70 °C, irradiation gives the cyclohexene complex $CpMn(CO)_2(C_6H_{10})$ and the monomeric vinylidene complex $CpMn(CO)_2CCH_2$. Clearly, $Cp_2Mn_2(CO)_4CCH_2$ does not function as a convenient vinylidene source under the conditions studied. Similar results were observed with norbornylene as a trapping reagent.



I



II



(1)

We are currently examining $Cp_2Mn_2(CO)_4CCH_2$ for evidence of nucleophilicity.

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Registry No. $Cp_2Mn_2(CO)_4(\mu$-$CCH_2)$, 71616-07-4; $CpMn(CO)_2(THF)$, 12093-26-4; C_2H_2, 74-86-2; $CpMn(CO)_3$, 12079-65-1.

Supplementary Material Available: A listing of calculated and observed structure factors and anisotropic thermal parameters (25 pages). Ordering information is given on any current masthead page.

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