Allene Formation within the Coordination Sphere. Synthesis and Crystal Structure of (C₅H₅)₂Mn₂(CO)₃(H₂CCCH₂)

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The synthesis of the title compound from $Cp_2Mn_2(CO)_4(CCH_2)$ by sequential treatment with $LiEt_3BH$ and CH_3I is described. The isomeric form of the C_3H_4 ligand and the detailed molecular structure have been established by an X-ray structure determination at −170 °C. The complex crystallizes in space group $P2_1/c$ with $a = 13.253$ (5) Å, $b = 15.768$ (7) Å, $c = 7.376$ (3) Å, and $\beta = 115.80$ (4)°. Refinement to a final R index of 0.054 and a final weighted R index of 0.077 has established the hydrocarbon as an allene unit symmetrically bridging a metal–metal bond of length 2.691(2) Å. This bond is also bridged by one carbonyl ligand. The carbon–carbon bond length in the allene moiety averages 1.394 Å, or 0.08 Å longer than in free allene.

Introduction

The dimer $Cp_2Mn_2(CO)_4(\mu\text{-}CCH_2)$ contains a $\mu\text{-}\eta^1$-vinylidene (C=CH₂) bridge whose carbon–carbon bond does not donate directly to either metal.[1] We have attempted to exploit this feature by carrying out reactions on this pendant "functional group". We have shown,[2] for example, that the vinylidene π-electron density will function as a base toward the proton; H^+ is added to the CH₂ carbon to generate $[CpMn(CO)_2]_2(\mu\text{-}CCH_3)^+$, in which the vinylidene has been transformed into a bridging carbyne.

It occurred to us that the vinylidene bridge might also tolerate addition of groups X and Y (not necessarily derived from the covalent addend X–Y), as shown formally in eq 1

$$mn_2(C{=}CH_2) + X\text{-}Y \longrightarrow mn_2\left(C{\overset{\displaystyle X}{\underset{\displaystyle CH_2Y}{<}}}\right) \qquad (1)$$
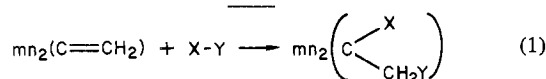
(mn is $CpMn(CO)_2$). This would demonstrate the relationship between the bridging vinylidene and alkylidene ligands. The prototype of such alkylidene complexes is $[CpMn(CO)_2]_2$-(CH₂),[3] which was, however, synthesized in a wholly different manner than shown in eq 1.

We report here the outcome of our attempts to sequentially add "H⁻" and then "CH₃⁺" to $[CpMn(CO)_2]_2(CCH_2)$, in an effort to produce $[CpMn(CO)_2]_2(C(H)Et)$.

Experimental Section

Synthesis of Cp₂Mn₂(CO)₃(C₃H₄). All operations were carried out in an atmosphere of purified nitrogen. $Cp_2Mn_2(CO)_4(CCH_2)$ (0.1 g, 0.26 mmol) was dissolved in 10 mL of dried (Na/K) THF at 25 °C. $LiBEt_3H$ (1 mL of a 1 M THF solution) was added (syringe) to a stirred solution of the vinylidene complex. The reaction, as monitored by IR spectroscopy, was complete (>90%) after 1 h. At this point CH_3I was added dropwise until gas evolution ceased. The solution was taken to dryness and subsequently dissolved completely in a minimum of toluene. Chromatography of this solution on Florisil (20 × 1 cm), eluting with toluene, yields two bands. The first (green) band was a minor component with a CO stretching frequency at 1850 cm⁻¹ (THF). A maroon band, the major product (Cp_2Mn_2-$(CO)_3C_3H_4$), eluted next. IR (THF): ν_{CO} 1910 (s), 1760 (s) cm⁻¹. ¹H NMR (C_6D_6): δ 3.79 (m, 1 H); 3.70 (s, 5 H); 2.71 (m, 1 H). Mass spectrum: $Cp_2Mn_2(CO)_xC_3H_4^+$ ($x = 3, 2, 0$); $Cp_2Mn_2(CO)_y^+$ ($y = 2$–0). Crystals suitable for the structural study were grown by layering heptane over a saturated solution of the complex in benzene.

Crystallography. Unit cell dimensions and other crystal data appear in Table I. Intensity data were collected at −170 °C in the range $4° \le 2\theta \le 50°$. Due to the small crystal size, no absorption corrections

(1) Folting, K.; Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1979**, *18*, 3483.
(2) Lewis, L. N.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 403.
(3) Herrmann, W. A.; Creswick, M.; Bernal, I. *J. Organomet. Chem.* **1979**, *172*, C39.

Table I. Crystal Data for $(C_5H_5)Mn_2(CO)_3(C_3H_4)$

empirical formula	$C_{16}H_{14}Mn_2O_3$
cryst dimens, mm	0.14 × 0.13 × 0.16
space group	$P2_1/c$
cell dimens (at −170 °C; 18 reflctns)	
a, Å	13.253 (5)
b, Å	15.768 (7)
c, Å	7.376 (3)
β, deg	115.80 (4)
molecules/cell	4
cell volume, Å³	1387.76
calcd density, g/cm³	1.743
wavelength, Å	0.710 69
molecular weight	364.16
linear abs coeff, cm⁻¹	17.54
total no. of reflctns collected	4235
total no. of unique intens	2446
total no. with $F > 0.0$	2339
total no. with $F > \sigma(F)$	2316
total no. with $F > 2.33\sigma(F)$	2198
final residuals	
$R(F)$	0.054
$R_w(F)$	0.077
goodness of fit for the last cycle	1.89
max Δ/σ for last cycle	0.15

were made. The data were processed in the usual manner,[4] and the structure was solved by using direct methods (LSAM). Hydrogen atoms were located in a difference Fourier and refined isotropically.

Fractional coordinates and equivalent isotropic thermal parameters appear in Table II. Anisotropic B's and structure factors are available as 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. Structural parameters derived from least-squares planes appear in Table V. All intermolecular contacts less than 3 Å involve hydrogen atoms as at least one of the participants. The shortest of these are H(1) to H(13) related by $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$ at 2.29 Å and H(2) to O(19) related by $\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} + z$ at 2.45 Å. Ring carbons deviate by less than 0.005 Å ($<1\sigma$) from their least-squares planes. Hydrogen positions deviate by less than 2σ to either side of these planes. Ring C–C distances vary by less than 3σ (average). Metal to ring-carbon distances vary by 0.029 Å (5σ) to Mn(1) and 0.050 (8σ) to Mn(2). Within the rings, the C–H separations average 0.90 Å, varying from 0.80 (7) to 1.09 (5) Å. Within the allene, the average C–H distance is 1.01 Å, ranging from 0.89 (6) to 1.12 (6) Å.

Results and Discussion

Synthesis and Spectroscopic Characterization. The reaction of maroon $Cp_2Mn_2(CO)_4(CCH_2)$ with 4 equiv (per dimer) of $LiEt_3BH$ in THF proceeds at a convenient rate above 0 °C to give a deep red solution which exhibits carbonyl stretching frequencies at 1878, 1855, 1828, and 1610 cm⁻¹; neither

(4) Data collection and reduction were carried out as previously reported: Visscher, M.; Huffman, J. C.; Streib, W. E. *Inorg. Chem.* **1974**, *13*, 793.

Table II. Fractional Coordinates and Thermal Parameters[a] for $(C_5H_5)_2Mn_2(CO)_3C_3H_4$

atom	10^4x	10^4y	10^4z	$10B_{iso}$
Mn(1)	3014 (1)	2770 (0)	7975 (1)	12
Mn(2)	3076 (1)	1087 (0)	7416 (1)	13
C(3)	2843 (4)	3323 (3)	10452 (7)	18
C(4)	3867 (4)	2854 (3)	11188 (7)	19
C(5)	4525 (5)	3223 (4)	10397 (8)	24
C(6)	3969 (5)	3909 (4)	9174 (9)	26
C(7)	2910 (5)	3967 (4)	9237 (8)	23
C(8)	1800 (4)	152 (3)	6328 (9)	24
C(9)	3111 (5)	252 (4)	5158 (9)	28
C(10)	2324 (5)	879 (3)	4187 (8)	22
C(11)	1484 (4)	826 (4)	4879 (8)	22
C(12)	2816 (5)	−198 (3)	6484 (8)	24
C(13)	3607 (5)	2698 (4)	5664 (9)	25
C(14)	3940 (4)	2051 (3)	7098 (8)	18
C(15)	4792 (4)	1500 (3)	8275 (10)	24
C(16)	2183 (4)	1794 (3)	8360 (8)	18
O(17)	1502 (3)	1678 (2)	8938 (6)	25
C(18)	1738 (4)	2990 (3)	5832 (8)	21
O(19)	909 (4)	3170 (3)	4456 (7)	34
C(20)	3739 (4)	736 (3)	9951 (8)	19
O(21)	4154 (3)	491 (2)	11600 (6)	26
H(1)	2296 (58)	3281 (37)	10647 (100)	26 (13)
H(2)	4042 (54)	2329 (45)	12115 (107)	35 (14)
H(3)	5187 (60)	3051 (35)	10567 (97)	24 (13)
H(4)	4045 (43)	4274 (35)	8785 (84)	7 (11)
H(5)	2384 (40)	4288 (30)	8727 (73)	3 (9)
H(6)	1299 (54)	−3 (40)	6846 (102)	30 (13)
H(7)	3849 (41)	135 (32)	4905 (78)	10 (9)
H(8)	2199 (46)	1322 (38)	3451 (91)	20 (11)
H(9)	826 (65)	1223 (47)	4262 (119)	37 (17)
H(10)	3283 (43)	−578 (32)	7307 (83)	14 (10)
H(11)	3017 (47)	2610 (36)	4482 (90)	15 (11)
H(12)	4162 (51)	3191 (34)	5465 (92)	23 (12)
H(13)	5416 (79)	1625 (57)	9766 (153)	66 (23)
H(14)	5126 (45)	1171 (32)	7560 (85)	12 (10)

[a] The isotropic thermal parameter listed for those atoms refined anisotropically is the isotropic equivalent. These appear without an esd.

Table III. Bond Distances (Å) in $Cp_2Mn_2(CO)_3C_3H_4$

Mn(1)–Mn(2)	2.691 (2)		
Mn(1)–C(13)	2.168 (5)	Mn(2)–C(15)	2.178 (5)
Mn(1)–C(14)	1.975 (5)	Mn(2)–C(14)	1.976 (5)
Mn(1)–C(16)	1.983 (5)	Mn(2)–C(16)	1.961 (5)
Mn(1)–C(18)	1.776 (5)	Mn(2)–C(20)	1.774 (5)
O(17)–C(16)	1.169 (6)		
O(19)–C(18)	1.160 (7)	O(21)–C(20)	1.161 (7)
C(13)–C(14)	1.396 (8)	C(14)–C(15)	1.389 (8)
Mn(1)–C(3)	2.124 (5)	Mn(2)–C(8)	2.121 (5)
Mn(1)–C(4)	2.140 (5)	Mn(2)–C(9)	2.140 (6)
Mn(1)–C(5)	2.144 (6)	Mn(2)–C(10)	2.170 (5)
Mn(1)–C(6)	2.153 (6)	Mn(2)–C(11)	2.165 (5)
Mn(1)–C(7)	2.135 (5)	Mn(2)–C(12)	2.120 (5)
C(3)–C(4)	1.428 (7)	C(8)–C(11)	1.435 (8)
C(3)–C(7)	1.383 (8)	C(8)–C(12)	1.413 (8)
C(4)–C(5)	1.372 (7)	C(9)–C(10)	1.388 (8)
C(5)–C(6)	1.396 (9)	C(9)–C(12)	1.396 (8)
C(6)–C(7)	1.426 (9)	C(10)–C(11)	1.415 (8)
average[a]	1.401 (25)		1.409 (18)

[a] Esd's on average values are calculated by using the scatter formula $\sigma(av) = [\Sigma(d_i - \bar{d})^2/(N - 1)]^{1/2}$ where d_i is one of N individual values and $\bar{d}$ is their average.

$Cp_2Mn_2(CO)_4CCH_2$ nor $CpMn(CO)_2CCH_2$ are evident in the infrared spectrum at this point. Methyl iodide is then added, causing immediate gas evolution (due in part to reduction of CH_3I by excess $LiEt_3BH$). After derivatization with methyl iodide, the THF solution exhibits IR bands at 1910, 1850, and 1760 cm^{-1}. Chromatography allows separation of a faster moving green band, which exhibits and IR stretch at 1850 cm^{-1} in THF, from a slower moving maroon band. The maroon

Table IV. Bond Angles (Deg) in $Cp_2Mn_2(CO)_3C_3H_4$[a,b]

C(13)–C(14)–C(15)	146.5 (5)		
Mn(1)–C(14)–Mn(2)	85.9 (2)	Mn(1)–C(16)–Mn(2)	86.1 (2)
Mn(1)–C(18)–O(19)	177.0 (5)	Mn(2)–C(20)–O(21)	178.4 (4)
Mn(1)–C(16)–O(17)	137.7 (4)	Mn(2)–C(16)–O(17)	136.2 (4)
Mn(2)–Mn(1)–C(13)	77.4 (2)	Mn(1)–Mn(2)–C(15)	76.0 (1)
Mn(2)–Mn(1)–C(14)	47.1 (1)	Mn(1)–Mn(2)–C(14)	47.0 (1)
Mn(2)–Mn(1)–C(16)	46.6 (1)	Mn(1)–Mn(2)–C(16)	47.3 (1)
Mn(2)–Mn(1)–C(18)	97.9 (2)	Mn(1)–Mn(2)–C(20)	100.4 (2)
C(18)–Mn(1)–M(1)	123.75	C(20)–Mn(2)–M(2)	121.64
C(18)–Mn(1)–CC(1)	93.88	C(20)–Mn(2)–CC(2)	93.20
M(1)–Mn(1)–CC(1)	124.54	M(2)–Mn(2)–CC(2)	126.13
M(1)–Mn(1)–C(16)	114.45	M(2)–Mn(2)–C(16)	115.87
M(1)–Mn(1)–Mn(2)	134.54	M(2)–Mn(2)–Mn(1)	134.44
CC(1)–Mn(1)–C(16)	107.60	CC(2)–Mn(2)–C(16)	106.48
CC(1)–Mn(1)–Mn(2)	62.29	CC(2)–Mn(2)–Mn(1)	61.47
CC(2)–Mn(1)–Mn(2)	44.45	CC(1)–Mn(2)–Mn(1)	44.10
Mn(1)–C(13)–H(11)	108.2 (36)	Mn(2)–C(15)–H(14)	110.3 (31)
Mn(1)–C(13)–H(12)	123.3 (30)	Mn(2)–C(15)–H(13)	126.7 (51)
C(14)–C(13)–H(11)	118.6 (37)	C(14)–C(15)–H(14)	115.6 (32)
C(14)–C(13)–H(12)	126.6 (31)	C(14)–C(15)–H(13)	125.6 (49)
H(11)–C(13)–H(12)	109.0 (48)	H(13)–C(15)–H(14)	109.0 (58)
C(16)–Mn(1)–C(18)	84.6 (2)	C(16)–Mn(2)–C(20)	84.4 (2)
C(13)–Mn(1)–C(18)	80.9 (2)	C(15)–Mn(2)–C(20)	79.1 (2)
C(14)–Mn(1)–C(16)	93.7 (2)	C(14)–Mn(2)–C(16)	94.3 (2)
C(13)–Mn(1)–C(14)	39.1 (2)	C(14)–Mn(2)–C(15)	38.7 (2)
Mn(1)–C(13)–C(14)	63.0 (3)	Mn(2)–C(15)–C(14)	62.8 (3)
Mn(1)–C(14)–C(13)	78.0 (3)	Mn(2)–C(14)–C(15)	78.5 (3)
Mn(1)–C(14)–C(15)	127.3 (4)	Mn(2)–C(14)–C(13)	130.0 (4)
C(4)–C(3)–C(7)	107.9 (5)	C(11)–C(8)–C(12)	108.0 (5)
C(3)–C(4)–C(5)	107.1 (5)	C(10)–C(9)–C(12)	110.3 (5)
C(4)–C(5)–C(6)	110.4 (5)	C(9)–C(10)–C(11)	107.7 (5)
C(5)–C(6)–C(7)	106.1 (5)	C(8)–C(11)–C(10)	107.0 (5)
C(3)–C(7)–C(6)	108.4 (5)	C(8)–C(12)–C(9)	107.0 (5)
average[c]	108.0 (16)		108.0 (14)

[a] M(i) denotes the midpoint of the Cp plane bound to Mn(i).
[b] CC(i) denotes the midpoint of the allene C=C bond bound to Mn(i). [c] See footnote *a*, Table III.

Table V. Distances and Angles Associated with Least-Squares Planes in $Cp_2Mn_2(CO)_3C_3H_4$

plane no.	atoms defining plane	atom	dist of atom from plane, Å
1	C(3)–C(7)	Mn(1)	1.776
2	C(8)–C(12)	Mn(2)	1.776
3	Mn(1)Mn(2)C(16)O(17)C(14)	Mn(1)	−0.02
		Mn(2)	−0.02
		C(16)	−0.01
		O(17)	0.02
		C(14)	0.03
4	C(13)C(14)C(15)		
5	Mn(1)C(13)C(14)		
6	Mn(2)C(14)C(15)		

plane no.	dihedral angles, deg	plane no.	dihedral angles, deg
1,2	10.10	3,4	50.97
1,3	45.25	5,6	61.98
2,3	46.13		

component exhibits carbonyl stretching bands at 1910 and 1760 cm^{-1}. The ^{1}H NMR spectrum of this compound contains a 10-proton resonance due to two equivalent Cp rings and two apparent triplets, each of intensity 2. The parent ion observed in the mass spectrum of this product is consistent with the formula $(C_5H_5)_2Mn_2(CO)_3(C_3H_4)$ (I), where C_3H_4 is only a "most probable" assignment for a mass 40 fragment which bears the four protons indicated by the ^{1}H NMR spectrum. In view of the unanticipated nature of this product and the equivocal nature of the C_3H_4 formulation, we turned to X-ray crystallography for clarification.

Description of the Structure. The X-ray diffraction study confirms that compound I is indeed $Cp_2Mn_2(CO)_3(C_3H_4)$, being composed of trans CpMnCO units bridged by one CO
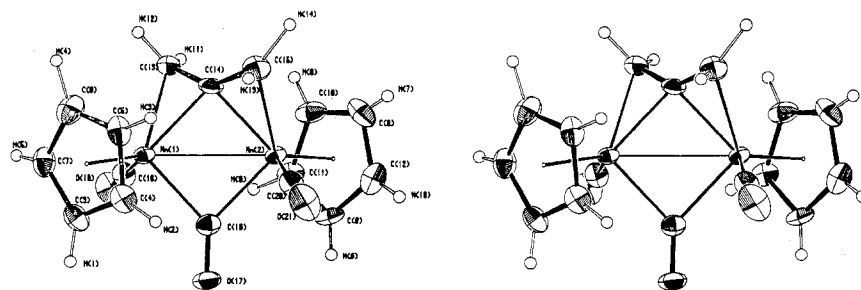
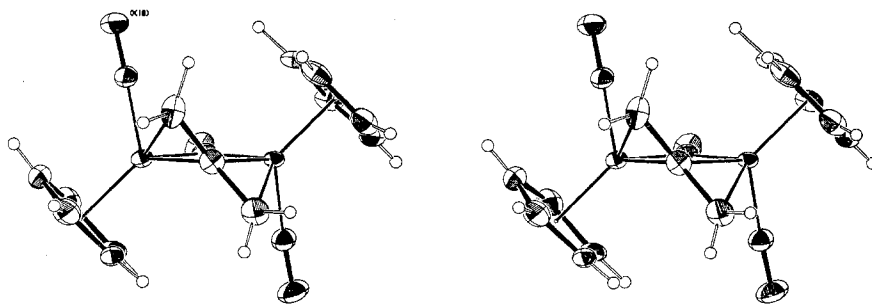**Figure 1.** Stereoscopic drawing of $Cp_2Mn_2(CO)_3C_3H_4$ viewed perpendicular to the plane Mn(1)Mn(2)C(14). The inequivalence of the allene protons is evident.

Figure 2. Stereoscopic drawing of $Cp_2Mn_2(CO)_3C_3H_4$ viewed down the noncrystallographic twofold rotational axis.

and by C_3H_4, which is an allene moiety.[5] These bridging groups flank a manganese–manganese bond of order 1 yielding an 18-electron configuration at each metal. The overall molecular structure is exceptionally faithful to twofold rotational symmetry; the C_2 axis passes through the atoms of the bridging carbonyl and the central allenic carbon. 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 (0.017 Å) occurs at oxygen of the carbonyl bridge. On consideration of the cyclopentadienyl ring midpoints rather than individual atoms, other deviations are all in the range 0.04–0.09 Å. As in $Cp_2Mn_2(CO)_4(CCH_2)$, the Cp ring planes in I are nearly parallel (dihedral angle 10.1°).

The arrangement of ligands about each metal atom is such as to produce equal (±2°) angles (124°) from the ring midpoint to the terminal carbonyl and to the allene double bond midpoint; the corresponding angle to the carbonyl bridge is 115° while that to the second metal is 134°.

The orthogonal π bonds in allene are optimized for bridging two metals (cf. $Cp_2Mo_2(CO)_4C_3H_4$)[6] when the allene axis is skewed (not orthogonal) with respect to the metal–metal line; each metal interacts with only one of the two allenic double bonds. In I, this skewing amounts to about 51° (Table V). If one were to formally replace the allene by two carbonyl ligands, each located at the center of one C=C bond of the diene, the resulting structure would closely reproduce those of $[CpMn(CO)_2]_2(\mu\text{-}B)$ (B = CH_2[3] or CCH_2[1]) and $[CpRe(CO)_2]_2(\mu\text{-}CO)$.[7] Thus, $Cp_2Mn_2(CO)_3(C_3H_4)$ resembles the methylene- and vinylidene-bridged manganese dimers by formal replacement of those bridges by CO. The torsional angle C(18)–Mn(1)–Mn(2)–C(20) is 147.0° in I; the carbonyl bridge resides within this "crevice". In $Cp_2Mn_2(CO)_4CCH_2$, the corresponding torsional angle is smaller (118.3°). This

difference arises since the allene ligand in I is more compact than the two terminal carbonyls of the vinylidene dimer. Manganese–manganese bonds symmetrically bridged by carbonyls are rare, as are cyclopentadienylmanganese carbonyl clusters. Another probable symmetrical CO bridge exists in $[CpMnCO(NO)]_2$[8] where NO/CO disorder prevented accurate structural definition. The single carbonyl bridge in $Mn_2(CO)_8(\mu\text{-}GeMe_2)(\mu\text{-}CO)$[9] exhibits a curious asymmetry in the Mn–C distance of 0.12 Å (12σ). The bridging carbonyl vibrational frequency in this dimer is 1835 cm⁻¹. The metal–carbon (μ-CO) bonds in I (1.972 Å) are shorter than those to μ-CH_2 (2.013 (5) Å) but comparable to those to μ-CCH_2 (1.975 (7) Å). In spite of this indication of strong bonding of the carbonyl bridge in I, as well as the low carbonyl stretching frequency (1760 cm⁻¹), the bridging and terminal CO bond lengths in I differ by less than 1σ.

The metal–metal bond length in I (2.691 Å) is somewhat shorter than in $[CpMn(CO)_2]_2(CH_2)$ (2.779 (1) Å),[3] $Mn_2(CO)_9(GeMe_2)$ (2.854(2) Å),[9] and $[CpMn(CO)_2]_2(CCH_2)$ (2.759 (2) Å)[1] but longer than that in $[CpMnCO(NO)]_2$ (2.571 (1) Å).[8] Given the diversity in type and number of bridging groups in the compounds cited, it is not inconsistent to consider all as having Mn–Mn single bonds. There are currently no isolable organometallic compounds possessing multiple Mn–Mn bonds.

The allene unit in $Cp_2Mn_2(CO)_3(C_3H_4)$ is distinctly bent at the central carbon as it is in all allene complexes.[10] This is a manifestation of the substituent bending (olefin nonplanarity) observed in all olefin complexes.[11,12] In I, and in $Cp_2Mo_2(CO)_4C_3H_4$[6] and $C_3H_4[RhCO(acac)]_2$,[14] the bending angle is within 1° of 145°; since the last compound contains

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(5) This structure should exhibit two infrared stretching frequencies in the terminal carbonyl region. The single observed band implies effective degeneracy or very low intensity for the second band.

(6) Bailey, W.; Chisholm, M. H.; Cotton, F. A.; Murillo, C.; Rankel, L. *J. Am. Chem. Soc.* **1978**, *100*, 802.

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(10) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245.

(11) Ittel, S.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.

(12) The allene hydrogens in I also bend away from the respective manganese atoms; both HCH angles decrease to 109° from the 118.4° characteristic of free allene.[13]

(13) Almenningen, A.; Bastiansen, O.; Traetteberg, M. *Acta Chem. Scand.* **1959**, *13*, 1699.

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no Rh–Rh bond, while the Mo–Mo bond is over 0.4 Å longer than the Mn–Mn bond in I, the bending angle of a bridging allene is quite insensitive to its environment.[15]   Another structural parameter is more responsive to such effects. Thus, it has been observed that the central carbon of a coordinated allene lies closer to the metal than does the terminal carbon. The difference between these metal–carbon bond lengths is 0.08 (7σ) Å in the dimeric rhodium complex,[14] 0.11 (4σ) Å in $Cp_2Mo_2(CO)_4C_3H_4$,[6] and 0.20 (40σ) Å in I. The carbon–carbon bond length in I (1.394 Å) is 0.08 Å longer than in allene itself (1.312 Å).[13]

Mass Spectral Fragmentation. The 70-eV electron impact mass spectrum of $Cp_2Mn_2(CO)_3(C_3H_4)$ indicates loss of a single CO ligand in overwhelming preference to loss of the allene fragment. The loss of allene or *two* carbonyls then become competitive paths. This contrasts with the mass spectral fragmentation of $Cp_2Mn_2(CO)_4(\mu_2\text{-}\eta^1\text{-}CCH_2)$,[1] in

which loss of *even numbers* of carbonyl ligands occurs to the exclusion of loss of the vinylidene ligand; vinylidene loss is seen only after the fragment $Cp_2Mn_2CCH_2^+$ has been achieved. This more facile loss of a four-electron donor allene compared to a two-electron donor vinylidene may at first appear paradoxical. In fact, it appears that this correlates with the lack of stability of the ejected fragment (i.e., vinylidene vs. allene), and therefore this could provide a spectroscopic probe for the mode of binding of isomeric hydrocarbon fragments (e.g., alkyne vs. vinylidene).

(15) The allene bending angle in a η^2 nonbridging environment[14] is 153°.

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Preparation and Characterization of MPSe₃(py)₁/ₙ Complexes

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$MPSe_3$ (M = Mn, Fe) reacts with pyridine molecules to form intercalation complexes. In the $MnPSe_3$–pyridine (py) system, two complexes of $MnPSe_3(py)_{1/3}$ and $MnPSe_3(py)_{1/4}$ were obtained, and a $FePSe_3(py)_{1/3}$ complex was prepared in the $FePSe_3$–pyridine system. From the results of one-dimensional electron density projections on the *c* axis, the arrangements of pyridine molecules between the $MnPSe_3$ layers were determined. The plane of the pyridine molecules is perpendicular to the $MnPSe_3$ layer for $MnPSe_3(py)_{1/3}$ but parallel for $MnPSe_3(py)_{1/4}$. The electrical resistivity of the complexes was closely related to the arrangements of pyridine molecules in the interlayers.

Introduction

In recent years, it was found that the superconducting transition temperature of some transition-metal dichalcogenides (MX_2) was strongly influenced by the absorption of pyridine molecules between the successive MX_2 layers.1–4 It has been said that metallic compounds with layer structures such as TaS_2 can form the charge-transfer-type complexes, but semiconductors such as MoS_2 are inert. Recently, however, it was found that the semiconductive FeOCl reacts with pyridine molecules to form intercalated compounds.[5]   This result indicates that some semiconductive inorganic layered compounds can react with pyridine molecules and the chemical-bond nature is quite different between MoS_2 and FeOCl. In order to conduct a further study on this problem, it is necessary to choose an appropriate semiconductive layered compound with strong covalent-bonding nature as a host material. The preparation and crystal structure of the host compounds $MPSe_3$ (M = Mn, Fe) have previously been reported by Klingen et al.[6,7] and Taylor et al.[8]   The structure

of the compounds is related to that of the layered transition-metal dichalcogenides MX_2, as shown in Figure 1. $MPSe_2$ (M = Mn, Fe) compounds are insulators ($\zeta \geq 10^8$ Ω cm) but intercalate some kinds of organic molecules with strong basicity. In the present investigation, we succeeded in forming intercalation compounds of $MPSe_3$–pyridine. The preparation and structure of the complexes are reported in this paper.

Experimental Section

Preparation of Host Compounds. For the preparation of $MnPSe_3$ and $FePSe_3$, Mn (99.99%), Fe (99.99%), P (99.99%), and Se (99.99%) powders were mixed in the desired ratio, sealed in evacuated silica tubes, and then heated at 650 °C for 1 week. After the reaction was completed, the reacted matter was cooled slowly to room temperature. Single crystals of $MPSe_3$ were grown by chemical vapor transport using iodine as a carrier gas. The chemical vapor transport reactions were carried out in a two-zone furnace with a temperature gradient (650–610 °C) for 1 week. The crystals obtained were hexagonal plates up to 0.1 × 3 × 3 mm³.

Preparation of Complexes. The reaction with pyridine was conducted in the closed system which was evacuated before the reaction.

In the case of the $MnPSe_3$–pyridine system, a complex (I) was obtained by heating $MnPSe_3$ at 30 °C for 4 days under the saturated vapor pressure of pyridine which was kept at room temperature. The complex (I) changed to another complex (II) by exposure to dry air for 1 day.

In contrast, $FePSe_3$ was less reactive with pyridine. The $FePS_3$–pyridine complex was obtained by heating $FePSe_3$ in distilled

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