Table II. Bond Lengths (Å) and Angles (Deg) in $[(C_5Me_5Rh)_3(CH)_2]$ (4)

Bond Lengths	
Rh(A)-Rh(B) = Rh(B)-Rh(C) etc.	2.6363 (5) Å
Rh(A)-C(1)	2.254 (6)
Rh(A)-C(2)	2.214 (6)
Rh(A)-C(3)	2.212 (6)
Rh(A)-C(4)	2.233 (6)
Rh(A)-C(5)	2.223 (6)
mean Rh-C(C_5Me_5)	2.227
Rh(A)-c.g. (C_5Me_5)	1.872
Rh(A)-C(11)	1.971 (17)
Rh(A)-C(12)	1.970 (19)
C(11)· · ·C(12)	2.502 (25)
Bond Angles	
Rh(A)-C(11)-Rh(B)	84.0 (8)
C(11)-Rh(A)-C(12)	78.8 (7)
Rh(A)-Rh(B)-Rh(C)	60.0 (4)

X-ray Crystal Structure Determination. Crystal data: $C_{32}H_{47}Rh_3$; $M = 740.44$, rhombohedral, $a = 11.918$ (7) Å, $\alpha = 101.91$ (4)°, $U = 1586$ Å^3, $Z = 2$, $D_{calcd} = 1.55$ g cm^{-3}, $F(000) = 748$, space group R_3 (C_{3i}^2, No. 148) (from systematic absences); Mo Kα radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo Kα) = 15.36 cm^{-1}.

Single-crystal X-ray data in the range $3.5 < 2\theta < 50°$ were collected on a Nicolet Instruments Syntex R3 four-circle diffractometer in the omega scan mode. A total of 1441 reflections with intensity $I > 3\sigma(I)$ and background difference of $\Delta < 4\sigma(B)$ were corrected for Lorentz and polarization but not for absorption or extinction. The structure was solved by Patterson and Fourier methods; block-diagonal-matrix least-squares refinement has reduced R to 0.027 at which stage all the thermal parameters of the non-hydrogen atoms are anisotropic, and those of the hydrogen atoms have fixed isotropic values.

The overall geometry of the molecule is shown in Figure 1; atomic coordinates are in Table I and distance and angle values in Table II.

Acknowledgment. We thank the S.E.R.C. and the Spanish Ministry of Education for support, the University of Sheffield for the award of a Junior Research Fellowship (P.M.B.) and Dr. W. Schäfer (Chemische Werke Hüls) and the Ethyl Corp. for gifts of chemicals.

Registry No. 2b, 80446-42-0; **4**, 83350-11-2; $(C_5Me_5Rh)_2Cl_4$, 83377-35-9; Al_2Me_6, 15632-54-9.

Supplementary Material Available: Tables of isotropic and anisotropic thermal parameters, hydrogen atom coordinates, and structure factors (39 pages). Ordering information is given on any current masthead page.

A Heterobinuclear Bridging Methylene Complex: Structures at −110 °C of Two Crystal Forms of (μ-Methylene)(μ-carbonyl)[(cyclopentadienylcarbonyliron)tetracarbonylmanganese], $(\mu\text{-CH}_2)(\mu\text{-CO})[\text{Cp(CO)FeMn(CO)}_4]$[†]

Steven M. Gadol[1] and Raymond E. Davis*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

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The novel heterobinuclear bridging methylene complex $(\mu\text{-CH}_2)(\mu\text{-CO})[\text{Cp(CO)FeMn(CO)}_4]$ (1) crystallizes in two forms: form A (from pentane), monoclinic, $P2_1/m$ (No. 11), $a = 8.282$ (1) Å, $b = 10.002$ (2) Å, $c = 8.504$ (1) Å, $\beta = 115.70°$ at −110 °C, $Z = 2$; form B (from thermal gradient vacuum sublimation), monoclinic, Cc (No. 9), $a = 15.402$ (2) Å, b = 6.1731 (7) Å, $c = 14.104$ (2) Å, $\beta = 107.36°$ at −110 °C, $Z = 4$. Single-crystal diffraction data (−110 °C) were used to determine and refine (by full-matrix least-squares methods) the crystal structures of both forms: form A, $R_1 = 0.036$, $R_2 = 0.037$ for 1251 reflections with $I/\sigma_I > 2.0$; form B, $R_1 = 0.038$, $R_2 = 0.041$ for 1774 reflections with $I/\sigma_I > 2.0$. Both forms contain disordered molecules with each bridging site occupied (exactly in form A and nearly in form B) by half of μ-CH$_2$ and half of μ-CO. Principal structural features of the molecule are (1) an unusually short Fe–C(μ) bond (average 1.921 Å), (2) the shortest Fe–Mn bond (average 2.615 Å) yet seen in an organometallic complex, (3) an unusually long Mn–C(μ) bond (average 2.087 Å), (4) an unsymmetrical bridge with Fe-X uncharacteristically shorter than Mn-X, and (5) Mn–CO(terminal) bond lengths which are significantly shorter when trans to μ-CH$_2$/CO than when trans to CO(terminal). These structural features are related to the strong π-acceptor nature of μ-CH$_2$ and μ-CO and to the presence on Fe and absence on Mn of the electron-releasing Cp group.

Introduction

Compounds containing unsubstituted (CH$_2$) or substituted (CHR, CR$_2$, or CRR′) methylene groups spanning two bonded transition-metal atoms have been the subject of many studies, involving synthesis, reactivity, spectroscopy, and theory, complemented by structural studies of a wide variety of these complexes.[2] Many of the bridging methylene complexes which have been structurally characterized have been substituted with either heteroatoms or aromatic rings (analogous to the mononuclear Fischer carbene complexes); several structures have been deter-

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[†] Dedicated to the memory of Rolly Pettit—mentor, colleague, friend.

(1) Robert A. Welch Foundation Undergraduate Scholar, 1979–1981.

(2) Some reviews and leading references: (a) Herrmann, W. A. "The Methylene Bridge", to appear in "Advances in Organometallic Chemistry". (b) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104. (c) Calderon, N.; Orstead, E. A.; Judy, W. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 401–409. (d) Hursthouse, M. B.; Jones, R. A.; Malik, K. M. A.; Wilkinson, G. J. *J. Am. Chem. Soc.* **1979**, *101*, 4128–4139. (e) Creswick, M.; Bernal, I.; Reiter, B.; Herrmann, W. A. *Inorg. Chem.* **1982**, *21*, 645–652. (f) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911–918. (g) Sumner, C. E., Jr.; Collier, J. A.; Pettit, R. *Ibid.* **1982**, *1*, 1350–1360. (h) Kao, S. C.; Thiel, C. H.; Pettit, R. *Organometallics*, submitted for publication.

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Table I. Crystallographic Summary

	form A	form B
	A. Crystal Data (−110 °C)[a]	
a, Å	8.282 (1)	15.402 (2)
b, Å	10.002 (2)	6.1731 (7)
c, Å	8.504 (1)	14.104 (2)
β, deg	115.70 (2)	107.36 (2)
V, Å^3	634.8	1279.9
d_{calcd}, g cm^{-3} (−110 °C)	1.871	1.856
empirical formula	$C_{12}H_7O_6FeMn$	$C_{12}H_7O_6FeMn$
fw	357.7	357.7
cryst system	monoclinic	monoclinic
space group	$P2_1/m$ (No. 11)	*Cc* (No. 9)
Z	2	4
F(000), electrons	356	712
	B. Data Collection (−110 °C)[b]	
radiation; λ, Å	Mo Kα; 0.710 69	Mo Kα; 0.710 69
mode	ω scan	ω scan
scan range	symmetrically over 1.0° about $K\alpha_{1,2}$ maximum	
background	offset 1.0 and −1.0° in ω from $K\alpha_{1,2}$ maximum	
scan rate, deg min^{-1}	1.0–5.0	2.0–5.0
exposure time, h	70.0	34.1
stability analysis		
computed *a*, *b*	0.0025 (5), −0.000 021 (8)	0.0005 (4), −0.000 016 (11)
max correction (on *I*)	7.0%	not applied
2*θ* range, deg	4.0–55.0	4.0–60.0
total reflctns measd	1537	1870
data cryst dimens, mm	0.11 × 0.43 × 0.27	0.12 × 0.19 × 0.44
data cryst vol, mm^3	0.0131	0.0133
data cryst faces	see footnote *c*	$(\bar{1}01)$, $(10\bar{1})$, $(\bar{1}\bar{1}1)$, $(\bar{1}11)$, $(\bar{1}00)$, and fragmentary face
absorption coeff, *μ*(Mo Kα), cm^{-1}	22.1	22.1
transmission factor range	0.567–0.785	0.616–0.789
	C. Structure Refinement[d]	
ignorance factor *p*	0.02	0.02
reflctns used, $I > n(\sigma_I)$	1251, 2.0	1774, 2.0
no. of variables	128	181
R_1, R_2	0.036, 0.037	0.038, 0.041
R_1 for all data	0.049	0.040
max shift/esd (non-H)	0.05	0.11
max shift/esd (H)	0.17	
max peak in diff map (e Å^{-3})	0.9	0.8

[a] Unit cell parameters for form A were obtained by least-squares refinement of the setting angles of 44 reflections with $22.0 < 2\theta < 26.5°$. For form B, 44 reflections with $24.2 < 2\theta < 26.9°$ were used. [b] Syntex $P2_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system. Data reduction was carried out as described in: Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B* **1976**, *B32*, 381. Crystal and instrument stability were monitored by remeasurement of four check reflections after every 96 reflections. These data were analyzed as detailed in: Henslee, W. H.; Davis, R. E. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1511. [c] Crystal faces had been noticeably rounded as the cold crystallization solution warmed, so faces could not be unambiguously indexed. [d] Relevant expressions are as follows, where in this footnote F_o and F_c represent, respectively, the observed and calculated structure factor amplitudes: function minimized was $\Sigma w(F_o - F_c)^2$, where $w = (\sigma_F)^{-2}$; $R_1 = \Sigma \text{abs}(F_o - F_c)/\Sigma F_o$; $R_2 = [\Sigma w(F_o - F_c)^2/\Sigma F_o^2]^{1/2}$.

mined for μ-CH_2 complexes with Os_2, Ru_2, Rh_2, and Mn_2 metal centers. Only a few structures have been studied,[3] however, which include methylene-like fragments bridging two different transition-metal atoms;[4-8] these have all involved at least one second- or third-row transition metal, and in each, the methylene bridge is substituted with aromatic and/or heteroatom groups. We report here the structure of $(\mu$-$CH_2)(\mu$-$CO)[(Cp)(CO)Fe$-$Mn(CO)_4]$ (*1*). This is, to our knowledge, the first structural account of a μ-CH_2 heterobinuclear complex; it also represents the first reported structural study of any μ-methylene complex, substituted or not, involving two different first-row transition metals. A preliminary account of the preparation, structure, and reactivity of this compound has been submitted.[9]

Experimental Section

Single crystals of 1 obtained by Dr. C. Thiel by very slow evaporation of a pentane solution at −20 °C were of adequate internal quality for X-ray studies, in spite of their poor external appearance. Attempts to produce better formed crystals by vacuum thermal gradient sublimation (0.050 torr, 55 °C to room temperature) gave crystals of excellent morphology, which, however, proved to be a second crystal form. The pentane form (space group $P2_1/m$) is herein referred to as form A, while the form produced by sublimation (space group *Cc*) is referred to as

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(3) Another rare example of a heterobinuclear μ-methylene complex, $(\mu$-$CH_2)Cp(CO)CoRh(CO)Cp$, has been reported, though apparently not studied by X-ray methods: Theopold, K. H.; Bergman, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 2489–2491.

(4) Howard, J. A. K.; Mead, K. A.; Moss, J. R.; Navarro, R.; Stone, F. G. A.; Woodward, P. A. *J. Chem. Soc., Dalton Trans.* **1981**, 743–750.

(5) Kreissl, F. R.; Friedrich, P.; Lindner, T. L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 314.

(6) Howard, J. A. K.; Jeffery, J. C.; Laguna, M.; Navarro, R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1981**, 751–762.

(7) Jeffery, J. C.; Moore, I.; Razay, H.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1981**, 1255–1258.

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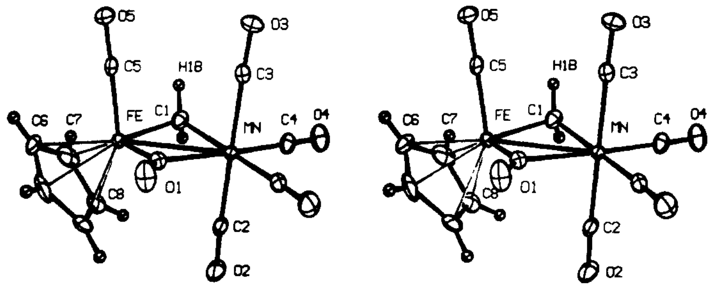

Figure 1. Stereoscopic view of the (μ-CH$_2$)(μ-CO)[Cp(CO)FeMn(CO)$_4$] molecule (1) in form A, illustrating the atom numbering scheme. The unlabeled H atom on C1 is H1A. On the disordered bridges, the atoms which are mirror related to O1, H1A, and H1B are omitted for clarity. Non-hydrogen atoms are shown as ellipsoids of 30% probability and hydrogen atoms as spheres of radius 0.1 Å.

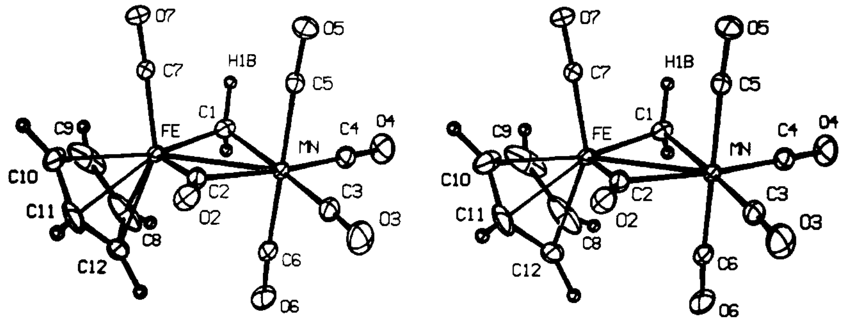

Figure 2. Stereoscopic view of the (μ-CH$_2$)(μ-CO)[Cp(CO)FeMn(CO)$_4$] molecule (1) in form B, illustrating the atom numbering scheme. The unlabeled H atom on C1 is H1A. On the disordered bridges, the atoms O1, H2A, and H2B are omitted for clarity. Non-hydrogen atoms are shown as ellipsoids of 30% probability and hydrogen atoms as spheres of radius 0.1 Å.

form B. X-ray experimental procedures were the same for crystals of these two forms.

A single crystal was mounted and transferred to a Syntex P2$_1$ autodiffractometer, where it was maintained in a cold (−110 °C) stream of dry nitrogen for the duration of the diffraction experiments. Preliminary diffraction studies revealed, in each case, diffraction symmetry and systematic absences prohibiting unequivocal space group assignment solely on these bases (vide infra). A summary of the pertinent crystal data and details of the X-ray diffraction data collection and processing is presented in Table I. Preliminary processing of the diffraction data was accomplished as described in detail previously,[10,11] including corrections for absorption based on measured crystal shape.

Each structure was solved by the heavy-atom method, using metal atom positions determined from a sharpened Patterson map. Because heavy-atom identity could not be ascertained at this early stage, each was included in the heavy-atom map calculation with the Fe scattering curve, and these atoms were identified following subsequent maps from consideration of their bonding environment. In the case of form A, since any reasonable estimate of bulk density indicated the presence of no more than two molecules per unit cell, the space group was initially assumed to be the more common $P2_1$ (No. 4). Early maps, however, revealed that the molecule was oriented in such a way as to be situated on the mirror plane (position *e*) of space group $P2_1/m$ (No. 11), with the mirror plane passing through the two heavy atoms, the Fe carbonyl group, two Mn carbonyl groups, and one Cp carbon. After a difference density map computed in P2$_1$ omitting the oxygen of the bridging carbonyl group revealed density consistent with one-half oxygen in these positions, the space group was taken to be $P2_1/m$. The subsequent successful refinement with this assumption is taken as confirmation of this choice of space group.

The expected presence of only four molecules per unit cell in Form B led to the initial assumption of one independent molecule per asymmetric unit in Cc (No. 9). The alternative space group consistent with the diffraction pattern, $C2/c$ (No. 15), would have required only half of a molecule per asymmetric unit. Since either of its sites of twofold symmetry (inversion center or twofold rotation axis) would have involved disorder of one or more carbonyl groups with the sterically quite different Cp ring, this was thought to be a very unlikely possibility. The near identity (at this early resolution) of the *y* coordinates of the two heavy atoms led to a quite cluttered heavy-atom map, though, so that several cycles of carefully interpreted electron and difference density maps were required to locate all non-hydrogen atoms in Cc. Again, the molecule is disordered, with the two bridging ligands interchanged in (approximately) half of the locations, though in this crystal form the disorder is not across a crystallographic symmetry element but rather within a molecule in a general position.

Both structures were refined by full-matrix least-squares methods, using the program SHELX. For form A, all non-hydrogen atoms were refined anisotropically, and all H atoms were refined isotropically, with fixed U = 0.025 Å. In the refinement of form B, considerable variation appeared in the geometry of the Cp ring, so this ring was constrained to a regular pentagon with C–C = 1.42 Å, with Cp H atom U values fixed at 0.05 Å; the CH$_2$ hydrogens (half-weight) did not behave well, so they were allowed to ride on the bridging C atoms with U = 0.025 Å. Additional details of the two refinements appear in Table I.

Tables II and III present final atomic coordinates (with esd's) and values of U or U_{eq}. Listings of thermal parameters and of observed and calculated structure factor amplitudes for both crystal structures are available.[12]

Discussion

The crystal structures of both forms consist of discrete molecules with no unusual intermolecular contacts. Figures 1 and 2 present stereoscopic views of single molecules

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(10) Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B* **1976**, *B32*, 381–386.

(11) Principal computer programs: least-squares lattice parameters, LSLAT by K. N. Trueblood; absorption correction, SYABS, a local version of ORABS by W. R. Busing and H. A. Levy as modified by J. M. Williams; full-matrix least squares and Fourier calculations, SHELX-76 by G. M. Sheldrick; least-squares planes, LSMP by M. E. Pippy; thermal ellipsoid plots, ORTEP-II by C. K. Johnson. Various data processing programs of local origin, including the following: statistical analysis of check reflections, SYSTD by T.-H. Hseu; data reduction, INCON by R. E. Davis; preparation of computer-typed tables of atomic parameters, bond lengths, bond angles and torsion angles for publication, FUER by S. B. Larson; and a listing of structure factor amplitudes, FTABLE by R. E. Davis. Neutral atom scattering factors used are from Table 2.2B, and anomalous dispersion corrections from Table 2.3.1: "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(12) Additional tables are available as supplementary material.

Table II. Fractional Coordinates and Thermal Parameters for Form A[a]

ATOM	X	Y	Z	U
FE	.28603(8)	.25	.41724(8)	.0202(2)
MN	-.04795(8)	.25	.18211(8)	.0189(2)
C1	.1413(4)	.4010(4)	.2953(5)	.0272(12)
O1	.1498(8)	-.0105(5)	.2994(8)	.043(2)
C2	-.1099(6)	.25	.3669(6)	.035(2)
O2	-.1546(5)	.25	.4747(5)	.067(2)
C3	.0127(6)	.25	-.0049(6)	.025(2)
O3	.0439(5)	.25	-.1221(4)	.042(2)
C4	-.2045(4)	.3872(4)	.0836(4)	.0271(11)
O4	-.2994(3)	.4755(3)	.0252(3)	.0426(10)
C5	.3912(6)	.25	.2765(6)	.025(2)
O5	.4635(4)	.25	.1877(4)	.0362(14)
C6	.5341(7)	.25	.6335(6)	.061(3)
C7	.4359(6)	.3644(5)	.6415(4)	.049(2)
C8	.2867(5)	.3182(4)	.6552(4)	.0385(14)
H1A	.114(10)	.457(9)	.354(10)	.03(2)
H1B	.191(10)	.458(9)	.245(10)	.04(2)
H6	.624(9)	.25	.622(8)	.06(2)
H7	.465(5)	.451(4)	.633(5)	.047(13)
H8	.194(6)	.378(5)	.650(5)	.067(14)

[a] See Figure 1 for identity of the atoms. Numbers in parentheses are estimated standard deviations in the units of the least significant digits for the corresponding parameter. [b] For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*A_{ij}$, where A_{ij} is the dot product of the *i*th and *j*th direct space unit cell vectors.

Table III. Fractional Coordinates and Thermal Parameters for Form B[a]

ATOM	X	Y	Z	U[b]
MN	.0	.17373(11)	.0	.0200(2)
FE	.16742(6)	.19780(11)	.11582(6)	.0222(2)
O1	.0549(7)	.5725(13)	.1245(6)	.036(3)
O2	.1371(5)	-.1562(11)	-.0258(6)	.036(3)
O3	-.0839(4)	-.1805(7)	-.1360(4)	.059(2)
O4	-.1571(3)	.4591(8)	-.0145(4)	.050(2)
O5	.0392(3)	.4205(7)	-.1666(3)	.0386(14)
O6	-.0460(3)	-.0459(11)	.1663(4)	.070(2)
O7	.2521(3)	.4417(7)	-.0115(3)	.044(2)
C1	.0728(3)	.4099(8)	.0973(4)	.0254(15)
C2	.1209(3)	-.0060(8)	.0105(4)	.0249(15)
C3	-.0528(4)	-.0413(9)	-.0852(5)	.034(2)
C4	-.0975(4)	.3462(9)	-.0111(4)	.030(2)
C5	.0262(3)	.3258(8)	-.1030(3)	.0240(14)
C6	-.0251(4)	.0316(11)	.1034(5)	.040(2)
C7	.2178(3)	.3486(8)	.0375(4)	.029(2)
C8	.1730(3)	.1763(8)	.2677(3)	.079(4)
C9	.2492(3)	.2925(8)	.2572(3)	.113(5)
C10	.2996(3)	.1512(8)	.2140(3)	.122(5)
C11	.2546(3)	-.0522(8)	.1977(3)	.053(3)
C12	.1764(3)	-.0367(8)	.2309(3)	.042(2)
H1A	.0517(3)	.4407(8)	.1565(4)	.025
H1B	.0828(3)	.5496(8)	.0662(4)	.025
H2A	.1455(3)	.0058(8)	-.0474(4)	.025
H2B	.1208(3)	-.1614(8)	.0305(4)	.025
H8	.1254(3)	.2344(8)	.2959(3)	.05
H9	.2647(3)	.4467(8)	.2768(3)	.05
H10	.3568(3)	.1885(8)	.1978(3)	.05
H11	.2745(3)	-.1834(8)	.1682(3)	.05
H12	.1315(3)	-.1551(8)	.2288(3)	.05

[a] See Figure 1 for identity of the atoms. Numbers in parentheses are estimated standard deviations in the units of the least significant digits for the corresponding parameter. [b] For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*A_{ij}$, where A_{ij} is the dot product of the *i*th and *j*th direct space unit cell vectors.

in the crystal forms and indicate the atom numbering schemes used in this paper. Bond lengths and angles appear in Tables IV and V.[12]

Ignoring the Fe–Mn bond, the coordination around Mn is octahedral, with two terminal CO ligands in the equatorial plane along with μ-CH_2 and μ-CO, and two terminal CO ligands axial. At the iron end of the molecule, again discounting the metal–metal interaction, the coordination may be described as roughly tetrahedral, with Cp, terminal CO, μ-CH_2, and μ-CO in the four sites. The central four-atom group is folded about the Fe–Mn line (12.3° in form A and 14.8° in form B, average 13.6°) in such a way as to relieve the nonbonded interactions between CO groups on the two metals. Thus, the distances C5···C3 =

Table IV. Bond Lengths (Å) and Angles (Deg) in Form A[a]

Atoms			Length	Angle
1	2	3	1 - 2	1-2-3
MN	FE	C1	2.6178(10)	52.00(10)
MN	FE	C5		98.71(12)
MN	FE	C6		170.7(2)
MN	FE	C7		134.79(14)
MN	FE	C8		106.96(10)
MN	FE	CPM		146.2(2)
C1	FE	C5	1.927(3)	90.6(2)
C1	FE	C6		128.41(9)
C1	FE	C7		92.7(2)
C1	FE	C8		90.3(2)
C1	FE	CPM		123.96(13)
C1	FE	C1 *1		103.16(14)
C1	FE	C7 *1		153.9(2)
C1	FE	C8 *1		120.4(2)
C5	FE	C6	1.759(6)	90.6(2)
C5	FE	C7		110.2(2)
C5	FE	C8		147.88(15)
C5	FE	CPM		115.1(3)
C6	FE	C7	2.080(4)	39.7(2)
C6	FE	C8		64.3(2)
C7	FE	C8	2.106(4)	37.7(2)
C7	FE	C7 *1		65.8(2)
C7	FE	C8 *1		63.7(2)
C8	FE	C8 *1	2.133(4)	37.3(2)
C1	MN	C2	2.087(3)	92.17(15)
C1	MN	C3		88.1(2)
C1	MN	C4		84.81(13)
C1	MN	FE		46.70(9)
C1	MN	C1 *1		92.70(13)
C1	MN	C4 *1		177.2(2)
C2	MN	C3	1.852(6)	179.6(2)
C2	MN	C4		89.22(15)
C2	MN	FE		86.66(12)
C3	MN	C4	1.864(6)	90.5(2)
C3	MN	FE		93.75(13)
C4	MN	FE	1.823(3)	131.02(10)
C4	MN	C4 *1		97.65(14)
FE	C1	MN		81.30(14)
02	C2	MN	1.128(8)	177.3(4)
03	C3	MN	1.133(7)	177.8(4)
04	C4	MN	1.143(4)	178.1(3)
05	C5	FE	1.150(7)	178.5(3)
C7	C6	FE	1.423(6)	71.1(2)
C7	C6	C7 *1		107.1(5)
C8	C7	FE	1.371(7)	72.2(2)
C8	C7	C6		106.7(4)
FE	C7	C6		69.2(2)
FE	C8	C7		70.1(2)
FE	C8	C8 *1		71.4(2)
C7	C8	C8 *1		109.7(4)
C8 *1	C8		1.363(6)	
01	C1 *1	FE	1.097(7)	138.5(3)
01	C1 *1	MN		139.6(4)

[a] See Figure 1 for identity of the atoms. Atoms identified by the notation *1 have been transformed by the operation (*x*, 0.5 − *y*, *z*). Numbers in parentheses are estimated standard deviations in the units of the least significant digits for the corresponding parameter. CPM designates the centroid of the five Cp carbons.

Table V. Bond Lengths (Å) and Angles (Deg) in Form B[a]

Atoms			Length	Angle
1	2	3	1 - 2	1-2-3
FE	MN	C1	2.6127(9)	46.55(14)
FE	MN	C2		46.25(13)
FE	MN	C3		128.3(2)
FE	MN	C4		131.3(2)
FE	MN	C5		93.19(13)
C1	MN	C2	2.085(5)	91.8(2)
C1	MN	C3		174.5(3)
C1	MN	C4		85.1(2)
C1	MN	C5		87.8(2)
C1	MN	C6		90.6(2)
C2	MN	C3	2.134(5)	82.8(2)
C2	MN	C4		175.1(2)
C2	MN	C5		85.9(2)
C2	MN	C6		94.7(2)
C3	MN	C4	1.812(6)	100.2(2)
C3	MN	C5		90.6(3)
C3	MN	C6		91.0(3)
C4	MN	C5	1.809(6)	90.2(2)
C4	MN	C6		89.1(3)
C5	MN	C6	1.872(5)	178.3(3)
C6	MN	FE	1.839(7)	86.2(2)
C1	FE	C2	1.919(5)	104.4(2)
C1	FE	C7		90.7(2)
C1	FE	CPM		122.3(2)
C1	FE	C8		88.9(2)
C1	FE	C9		99.0(2)
C1	FE	C10		136.6(2)
C1	FE	C11		153.3(2)
C1	FE	C12		115.9(2)
C1	FE	MN		52.09(14)
C2	FE	C7	1.916(5)	89.6(2)
C2	FE	CPM		119.8(2)
C2	FE	C8		129.4(2)
C2	FE	C9		154.1(2)
C2	FE	C10		118.9(2)
C2	FE	C11		88.5(2)
C2	FE	C12		93.9(2)
C2	FE	MN		53.6(2)
C7	FE	CPM	1.789(6)	122.2(2)
C7	FE	C8		139.6(2)
C7	FE	C9		101.2(2)
C7	FE	C10		88.0(2)
C7	FE	C11		113.0(2)
C7	FE	C12		151.1(2)
C7	FE	MN		99.9(2)
CPM	FE		1.748(4)	
CPM	FE	MN		137.8(2)
C8	FE	C9	2.122(5)	39.3(2)
C8	FE	C10		65.7(2)
C8	FE	C11		65.2(2)
C8	FE	C12		38.8(2)
C8	FE	MN		111.29(13)
C9	FE	C10	2.099(4)	39.4(2)
C9	FE	C11		65.6(2)
C9	FE	C12		65.5(2)
C9	FE	MN		144.15(15)
C10	FE	C11	2.112(4)	39.0(2)
C10	FE	C12		65.2(2)
C10	FE	MN		168.65(14)
C11	FE	C12	2.144(5)	38.6(2)
C11	FE	MN		129.69(13)
C12	FE	MN	2.149(5)	105.24(12)
C1	01		1.137(10)	
C2	02		1.122(9)	
C3	03		1.130(7)	
C4	04		1.142(7)	
C5	05		1.137(7)	
C6	06		1.136(9)	
C7	07		1.142(8)	
MN	C1	FE		81.4(2)
MN	C1	01		134.6(6)
FE	C1	01		143.8(6)
MN	C2	FE		80.1(2)
MN	C2	02		134.9(5)
FE	C2	02		144.4(5)
MN	C3	03		177.6(5)
MN	C4	04		177.2(5)
MN	C5	05		177.7(4)
MN	C6	06		174.9(6)
FE	C7	07		178.1(4)
C9	C8	C12	1.420(7)	108.0(5)
C9	C8	FE		69.5(3)
C12	C8	FE	1.420(7)	71.6(3)
C10	C9	FE	1.420(7)	70.8(3)
C10	C9	C8		108.0(4)
FE	C9	C8		71.2(3)
C11	C10	FE	1.420(7)	71.7(2)
C11	C10	C9		108.0(4)
FE	C10	C9		69.8(2)
C12	C11	FE	1.420(8)	70.9(3)
C12	C11	C10		108.0(4)
FE	C11	C10		69.3(3)
FE	C12	C8		69.5(3)
FE	C12	C11		70.5(3)
C8	C12	C11		108.0(4)

[a] See Figure 1 for identity of the atoms. Numbers in parentheses are estimated standard deviations in the units of the least significant digits for the corresponding parameter. CPM designates the centroid of the five Cp carbons.

3.010 (7) Å in form A and C5···C7 = 3.028 (7) Å in form B put these groups at the outer limit of the collision diameter range of 2.75–3.00 Å said to be appropriate for the van der Waals' interactions between carbonyls in binuclear complexes.[13] The shortest nonbonded contacts between carbonyl on Mn and Cp carbon on Fe are comfortable—C2···C8 = 3.206 (7) Å in form A and C6···C12 = 3.117 (8) Å in form B.

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Both crystal forms contain disordered molecules of 1; as described above, this disorder has the effect that each bridging position is occupied (exactly in form A and nearly in form B) on average by half of $\mu\text{-CH}_2$ and half of μ-CO. Such disorder in $(\mu\text{-CH}_2)(\mu\text{-CO})$ complexes seems to be a common occurrence (e.g., $(\mu\text{-CH}_2)(\mu\text{-CO})_2\text{Fe}_2(\text{CO})_6$[15] and $(\mu\text{-CH}_2)(\mu\text{-CO})\text{Os}_2(\text{CO})_{10}$[16]), though not an invariable one (e.g., $(\mu\text{-CO})(\mu\text{-CH}_2)(\text{Me}_2\text{Cp})_2\text{Co}_2$[17] and $(\mu\text{-CO})(\mu\text{-CH}_2)\text{Cp}_2\text{Fe}_2(\text{CO})_2$[18]). The only significant difference observed in the molecular structures in the two forms is a small rotation of the Cp ring in form B away from the symmetric conformation seen in form A. Of course, the disorder present in both forms, while permitting resolution only of the μ-carbonyl O atoms and the μ-methylene H atoms, implies lack of strict coincidence of the other atoms as well. Thus, the "thermal parameters" which are considerably higher for both crystal forms in, e.g., the carbonyl group and the Cp ring on Fe and the "axial" carbonyls on Mn, than would be expected at −110 °C, surely represent the effects of this disorder. Nevertheless, the principal metrical details of this novel complex are sufficiently well determined to merit report and some comment. In particular, the thermal ellipsoids of the bridging carbon atoms (C1 in form A and C1 and C2 in form B) are among the smallest and most symmetrical in the structures, suggesting that, in fact, these two bridging groups do display, in this complex, very similar bond lengths and bridging angles. It is to be hoped that subsequent structural studies of well-ordered heterobinuclear $\mu\text{-CH}_2$ complexes will further clarify such details.

The composite of bond lengths in the central four-atom fragment is quite consistent with generalizations which have been discussed both on experimental grounds by Herrmann et al.[2a,e,19] and on theoretical grounds by Hoffmann et al.[20] The principal conclusions of those discussions which apply here are (1) that $\mu\text{-CH}_2$ is a quite good π acceptor, comparable to μ-CO, (2) that bridging by stronger π acceptors such as CH_2 or CO serves to enhance the bonding in the bridge region, and (3) that the presence of a Cp ring in place of terminal CO ligands strengthens the bridge bonding, making the metal atom a better donor. The Fe–C(μ) bond in 1 is very short (1.927 (3) Å in form A and 1.919 (5) and 1.916 (5) Å in form B, average 1.921 Å) compared to 2.015 (1) Å in $(\mu\text{-CH}_2)(\mu\text{-CO})_2\text{Fe}_2(\text{CO})_6$,[15] which does not contain Cp (but in which the bridge position is disorderd $(\mu\text{-CH}_2)_1{:}(\mu\text{-CO})_2$) and to 1.987 (1) Å in $(\mu\text{-CHMe})(\mu\text{-CO})[\text{CpFe(CO)}]_2$[15,21] and 1.952 Å (average of four) in $(\mu\text{-CO})(\mu\text{-CHCO}_2\text{-}t\text{-Bu})[\text{CpFe(CO)}]_2$,[22] both of which contain Cp rings on Fe. By contrast the Mn–C(μ) bond in 1 is longer (2.087 (3) Å in form A and 2.085 (5) and 2.134 (5) Å in form B, average 2.102 Å) than the reported value of 2.014 Å (av) in $(\mu\text{-CH}_2)[(\text{MeCp})\text{Mn(CO)}]_2$;[2e] it compares favorably with the average Mn–CO(μ) distance of 2.095 Å in the asymmetric (2.037, 2.154 Å) bridge in $(\mu\text{-CO})(\mu\text{-GeMe}_2)[\text{Mn(CO)}_4]_2$,[14] which is apparently the only structurally characterized $(\mu\text{-CO})\text{-Mn}_2$ compound. This is, of course, consistent with the decreased availability of back-bonding electron density at metals on which the other ligands include only CO and not Cp.

A further indication of the strengthened bonding in the bridging region is the remarkably short Fe–Mn distance (2.618 (1) Å in form A and 2.613 (1) Å in form B, 2.615-Å average). This may be compared, among organometallics, to 2.84 Å in the nonbridged $\text{Cp(CO)}_2\text{FeMn(CO)}_5$,[23] 2.848 (4) Å in $(\mu\text{-AsMe}_2)(\text{CO})_4\text{FeMn(CO)}_4$,[24] 2.825 (5) Å in $(\mu\text{-PPh}_2)(\text{CO})_4\text{FeMn(CO)}_4$,[25] 2.760 (4) Å in $(\mu\text{-C}{=}\text{CHPh})(\text{CO})_3\text{FeMnCp(CO)}_2$,[26] and 2.742 (4) and 2.752 (4) Å in the cluster compound $\text{PhP}[(\text{CO})_6\text{Fe}_2\text{MnCp}(\mu\text{-CO})_2]$.[27] The Fe–Mn bond observed in this work is, however, not as short as has been reported for certain alloys, cf. 2.559 Å in $\text{Fe}_3\text{Mn}_4\text{Ge}_6$[28] and 2.324 in $\text{Fe}_4\text{Mn}_{77}\text{Si}_{19}$.[29] As has been carefully discussed by Bernal and Herrmann et al.,[2e] observed Mn–Mn lengths (and, by implication, perhaps Mn bond lengths to other transition metals ?) are exceptionally sensitive to many features of their bonding environment, including the number and nature of bridging ligands. The present compound seems to be the only structurally studied bis bridged Fe–Mn compound, and both these bridges are quite good π acceptors.

An additional feature of the bridging in this structure which requires comment is its unsymmetrical nature. All previous (μ-X)Fe–Mn structures have exhibited either Fe–X > Mn–X (viz., 2.33 (2) vs. 1.76 (2) Å and 2.44 (2) vs. 1.76 (2) Å (semibridging carbonyls ?) in the cluster compound $\text{PhP}[(\text{CO})_6\text{Fe}_2\text{MnCp}(\mu\text{-CO})_2]$[27]) or FeX ≈ Mn–X (viz., 2.239 (6) vs. 2.257 (6) Å in $(\mu\text{-PPh}_2)(\text{CO})_4\text{FeMn(CO)}_4$;[25] 2.356 (3) vs. 2.350 (3) Å in $(\mu\text{-AsMe}_2)(\text{CO})_4\text{FeMn(CO)}_4$[24]). In 1, the pattern is reversed, with Fe–C vs. Mn–C lengths of 1.927 (3) vs. 2.087 (3) Å in form A and 1.919 (5) and 1.916 (5) vs. 2.085 (5) and 2.134 (5) Å in form B (average Fe–C = 1.921 (4) vs. Mn–C = 2.102 (4) Å or Fe–C < Mn–C by 0.181 Å). The origin of this variation may again be the electron-releasing effect of the Cp ring, since in the unsymmetrically bridged compounds, the shorter bond is to the metal atom carrying the Cp ring, while the μ-P[25] and μ-As[24] ligands symmetrically bridge two different M(CO)_4 groups. This is substantiated by the pattern of bond lengths in the heterobinuclear complexes $(\mu\text{-C(OMe)(C}_6\text{H}_4\text{-Me-4))Pt(PMe}_3)_2\text{W(CO)}_4(\text{PMe}_3)$,[4] $(\mu\text{-C(OMe)(Ph))Pt(PMe}_3)_2\text{W(CO)}_5$,[8] and $(\mu\text{-C(CO}_2\text{Me)(Ph))Pt(PMe}_3)_2\text{Cr(CO)}_4(\text{PMe}_3)$,[6] in which the shortest M–C(μ) invariably involves the metal with the largest number of highly electron-releasing PR_3 groups, their effect apparently overriding the covalent radii of the metal atoms.

The Fe–C(μ)–Mn angle in 1 averages 80.9 (2)° (81.3 (1)° in form A and 80.1 (2) and 81.4 (2)° in form B), centered in the extreme range of 81 ± 7° cited in Herrmann's review[2a] and within the 76–81° range he describes as typical. Further, it coincides with the average value (80.9°) in Table VII of ref 2e for seven Fe_2, Co_2, and Rh_2 structures. The

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H–C–H angle in form B was constrained in the refinement to be 109.5°, while its calculated value after the refinement of form A was 98 (9)°. However, these hydrogen positions are quite poorly determined, since they were refined as half-weight hydrogen atoms in the proximity (approximately 0.8 Å) of the disordered carbonyl oxygen, so no conclusions regarding H–C–H or M–C–H angles should be drawn from the results reported here.

In the few structures in which metal geometry is such that one terminal CO group is clearly trans to μ-CR_2 (where R can be H), patterns of M–C bond lengths seem to be emerging which suggest that μ-CR_2 may be, in fact, a slightly poorer π acceptor than μ-CO. For example, in three heteronuclear μ-carbene complexes reported by Stone and co-workers, the following M–CO(terminal) bond lengths are seen: in $(\mu\text{-}C(OMe)(C_6H_4\text{-}Me\text{-}4))Pt(PMe_3)_2W(CO)_4)(PMe_3)$[4]—W–CO trans to μ-CR_2 = 1.96 (2) Å, trans to PMe_3 = 1.95 (1), and trans to CO = 2.02 (2) and 2.03 (2) Å; in $(\mu\text{-}C(OMe)(Ph))Pt(PMe_3)_2W(CO)_5$[8]—W–CO trans to CR_2 = 1.99 (1) Å and trans to CO = 2.03 (1), 2.04 (1), 2.06 (1), and 2.07 (2) Å; in $(\mu\text{-}C(CO_2Me)(Ph))Pt(PMe_3)_2Cr(CO)_4(PMe_3)$[6]—Cr–CO trans to μ-CR_2 = 1.85 (4) Å, trans to PMe_3 = 1.75 (5) Å (semibridging), and trans to CO = 1.86 (5) and 1.93 (5) Å. Thus, in these complexes, M–CO trans to μ-CR_2 tends to be shorter than M–CO trans to other carbonyls. Two features which complicate the extrapolation to comparison of μ-CR_2 and μ-CO are that (1) these complexes do not contain μ-CO for direct comparison and (2) these μ-CR_2 bridges all carry aromatic or O-containing substituents and may thus not be strictly comparable to μ-CH_2 or μ-CR_2 where R = alkyl.

Further, though still not definitive, structural indications along these lines are seen in 1 and in $(\mu\text{-}CH_2)(\mu\text{-}CO)_2Fe_2(CO)_6$.[15] In the latter structure, the small but perhaps marginally significant decrease in the Fe-CO(terminal) bond lengths compared to those in $Fe(CO)_9$[30] was viewed as a consequence of strengthening the Fe-CO(terminal) bonding due to the substitution of the slightly poorer π-acceptor μ-CH_2 for μ-CO.[15] In similar fashion in 1, the Mn–CO bonds trans to μ-CH_2/CO are distinctly shorter (1.823 (3) Å in form A and 1.809 (5) and 1.812 (6) Å in form B, average 1.815 Å) than those trans to terminal CO (1.852 (6) and 1.864 Å in form A and 1.839 (6) and 1.872 (5) Å in form B, average 1.857 Å). These latter values may be compared with, e.g., the values for the seven Mn–CO lengths not trans to Mn–Mn in the nonbridged $Mn_2(CO)_9(CPh(OMe))$[31]—average = 1.847 Å and range = 1.832–1.856 Å—in which the Mn–CO length trans to the (terminal) carbene is 1.979 (5) Å. Unfortunately, due to the disorder present in both 1 and in $(\mu\text{-}CH_2)(\mu\text{-}CO)Fe_2(CO)_6$,[15] the terminal CO positions obtained by refinement are the weighted averages of those actually trans to μ-CH_2 and those trans to μ-CO, weighted as 1:1 in 1 and as 1:2 in the Fe_2 structure. A careful determination of an ordered structure (preferably not involving Cp or phosphines—vide supra) in which one terminal CO is clearly trans to μ-CH_2 and one is clearly trans to μ-CO should help to clarify this point.

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Registry No. 1, 83350-15-6.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes, anisotropic thermal parameters, and bond lengths and angles involving hydrogens (21 pages). Ordering information is given on any current masthead page.

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Preparation and Properties of Some Carbonyl-Bridged Dinuclear Copper Complexes†

G. Doyle,* K. A. Eriksen, M. Modrick, and G. Ansell

Corporate Research, Exxon Research and Engineering Company, Linden, New Jersey 07036

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Several complexes of the type $(diamine)_2Cu_2(CO)(O_2CR)^+X^-$, which contain both a carbonyl and a carboxylate group bridging two coppers, have been prepared. The preferred method of synthesis involves the reaction of $Tl(O_2CR)$ and (diamine)CuI under a CO atmosphere. All the complexes are characterized by a CO absorption in the infrared at approximately 1900–1950 cm^{-1}. A related compound, $(tmed)_2Cu_2(CO)C_4O_4$, which contains a bridging squarate group, was also prepared and the structure of its CH_2Cl_2 solvate characterized by single-crystal X-ray diffraction. The geometry of the squarate complex is quite similar to that of the benzoate derivative in spite of the charge difference and the much larger "bite" of the squarate ligand compared to the benzoate group.

Introduction

In a recent publication by Floriani's group in Pisa[1] a novel binuclear copper(I) complex was described in which the copper atoms are bridged by a single CO molecule as well as by a benzoate ion. This represents the only known complex of copper with a bridging CO although a few other binuclear copper complexes with terminal CO groups are known[2-7] There is also at least one example of what

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† Dedicated to the memory of Rowland G. Pettit.

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