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Crystal Structures at -35 °C of the Unsubstituted and Substituted Bridging Methylene Complexes $Fe_2(CO)_8(\mu\text{-}CH_2)$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$

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The structures of the unsubstituted and substituted bridging methylene complexes $Fe_2(CO)_8(\mu\text{-}CH_2)$ (**1**) and $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**2**) have been determined by single-crystal X-ray diffraction techniques with three-dimensional data collected at -35 °C by counter methods. Diffraction data (with the same single crystal) were also acquired for **1** at 22 °C so that its structure could be compared with that of the isostructural complex $Fe_2(CO)_9$, which was determined at 22 °C elsewhere. Pale yellow hexagonal prisms of **1** form in space groups $P6_3/m$ with two molecules within a unit cell of dimensions $a = 6.4631$ (6) and $c = 15.911$ (4) Å at -35 °C and $a = 6.502$ (2) and $c = 15.965$ (12) Å at 22 °C. The calculated density of 1.989 g cm^{-3} at 22 °C for $Z = 2$ agrees with the measured value of 1.94 g cm^{-3}. Red, elongated prisms of **2** crystallize in orthorhombic space group *Pnma* with unit cell constants at -35 °C $a = 15.125$ (3), $b = 14.448$ (3), and $c = 6.355$ (1) Å which agree with the values recently communicated for this structure by other workers. Full-matrix least-squares refinements of the structures have converged with conventional *R* indices (on $|F|$) of 0.027 for **1** with use of 664 and 611 observations with $I_o/\sigma(I_o) > 3.0$ for the -35 and 22 °C data sets and 0.032 for **2** with use of 1208 similarly selected reflections. The crystal structures of **1** at -35 and 22 °C are identical and isostructural with that of $Fe_2(CO)_9$. Thus, the molecules occupy sites of C_{3h} symmetry and are thereby disordered such that the bridging positions of **1**, which are equivalent by the C_3 axis of the molecule (or the $\bar{6}$ axis of the crystal), are statistically $^2/_3$ of a CO ligand and $^1/_3$ of a CH_2 ligand. The only additional structural differences between **1** and $Fe_2(CO)_9$ are the small decreases in the lengths of the Fe–Fe and Fe–CO (terminal) bonds following coordination of the bridging CH_2 ligand. The structure of **2**, as determined in this laboratory, is consistent with that recently reported (see above) and is also in excellent agreement with common structural features of *cis*-$[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)_2$.

Introduction

Compounds containing unsubstituted or substituted methylene groups spanning two bonded transition-metal atoms have begun to appear in the literature. These include complexes of CH_2 with Os_2, Ru_2, Rh_2, and Mn_2 metal centers as well as complexes of CRR′ with Mn_2, Re_2, Fe_2, Co_2, and Rh_2 atoms. (A Pt-μ-CRR′-Pt complex, in which a Pt-Pt bond is not formed, and a heteronuclear Ti-μ-CH_2-Al complex have also been reported.)[1,2] Recently, the preparation, crystallographic characterization, and preliminary explorations of the chemical reactivity of the simple species $Fe_2(CO)_8(\mu\text{-}CH_2)$ (**1**) were communicated.[3]

Bridging methylene complexes are of interest primarily because they may be regarded as models of the intermediates which form on metal surfaces in heterogeneous reactions such as those which presumably exist in Fischer–Tropsch hydrocarbon polymerizations. Herein, therefore, we report in full the details of the crystal structure of **1** at -35 °C and in addition at 22 °C, to allow comparison of the structure of **1** with that of the metal carbonyl $Fe_2(CO)_9$.[4,5] In addition, we also present an account of the crystal structure at -35 °C of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**2**) which has been prepared and studied by Pettit and Lu[6] as an extension and modification of the chemical utility of complexes akin to **1** and to many of those referenced above. Following the preparation of this manuscript, a preliminary report of the synthesis and crystal structure of **2** was published by other workers.[7] Accordingly, the description of the crystallographic study of **2** in our laboratory has been abbreviated and is presented here to complement the discussion of the structure of the unsubstituted bridging CH_2 complex **1**.

Experimental Section

Excellent single crystals of **1** obtained as pale yellow hexagonal prisms from an ethyl acetate solution at ca. 10 °C were supplied by Professor R. Pettit. A well-formed crystal was mounted approximately along its hexagonal axis and then transferred to a Syntex P2$_1$ automated diffractometer equipped with an inert-gas delivery system which maintained the crystal in a stream of cold (-35 °C), dry nitrogen during the course of initial diffraction experiments and the collection of data at the lower temperature. The delivery system was not used during the collection of data (with the same crystal) at room temperature. Preliminary examination showed the crystal to have the symmetry and systematic reflection absences consistent with hexagonal space groups $P6_3$ (No. 173) and $P6_3/m$ (No. 176) and unit cell parameters virtually identical with those of crystalline $Fe_2(CO)_9$.[4,5] Hence, the crystal structures of **1** and $Fe_2(CO)_9$ are "isostructural", although that of **1**, as discussed below, is disordered. Crystal data for **1** are given in Table I. Two data sets, one at -35 °C and another at 22 °C, were gathered essentially as described by Cotton and Troup[5] for the structure of $Fe_2(CO)_9$. A summary of the details of data collection is presented in Table I. The measured X-ray diffraction intensities were reduced and assigned standard deviations (with $p = 0.02$) as described previously.[8]

Elongated prismatic, red crystals of **2**, grown from ethyl acetate solution at ca. 10 °C, were provided by Lu and Pettit. Exploratory examination of a suitable specimen with the diffractometer indicated orthorhombic symmetry consistent with space groups $Pna2_1$ (No. 33) and *Pnma* (No. 62). Crystal data and data collection details are available in Table I. The intensity data were reduced as outlined above.

Solution and Refinement of the Structures. Full-matrix least-squares refinements of the crystal structures of **1** (at -35 and 22 °C) were initiated with use of the positional parameters reported for the structure of $Fe_2(CO)_9$.[5] The structure of **2** was solved by standard heavy-atom methods and then refined by full-matrix least-squares procedures.[9] The function minimized in refinement is $\sum w(|F_o| - |F_c|)^2$, where the weight w is $\sigma(|F_o|)^{-2}$, the reciprocal square of the standard deviation of each observation, $|F_o|$. Neutral-atom scattering factors for Fe, O, C,[10] and H[11] were used in these calculations, and the real ($\Delta f'$) and

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(1) See the extensive list of references which accompanies the report of the Ru_2 complexes: Hursthouse, M. B.; Jones, R. A.; Malik, K. M. A.; Wilkinson, G. *J. Am. Chem. Soc.* **1979**, *101*, 4128.

(2) In addition to the Fe_2 complex cited in ref 1, the complex $Fe_2(CO)_8(\mu\text{-}CH(C_6H_4(OCH_3)))$ was prepared and characterized chemically and crystallographically in 1973: Blankenship, L. T.; Davis, R. E.; Pettit, R., unpublished results.

(3) Sumner, C. E., Jr.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 1752.

(4) Powell, H. M.; Ewens, R. V. G. *J. Chem. Soc.* **1939**, 286.

(5) Cotton, F. A.; Troup, J. M. *J. Chem. Soc., Dalton Trans.* **1974**, 800.

(6) Lu, P.; Pettit, R., unpublished results.

(7) Dyke, A.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1980**, 441. The synthetic route reported in this reference is different from that of Lu and Pettit.[6]

(8) Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B* **1976**, *32*, 381.

(9) A listing of principal computer programs used in these studies is available in ref 8.

(10) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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Table I. Crystallographic Summary[a]

	$Fe_2(CO)_8(\mu\text{-}CH_2)$		$[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$
	−35 °C	22 °C	−35 °C
	Crystallographic Data		
a, Å	6.4631 (6)	6.502 (2)	15.125 (3)
b, Å	6.4631 (6)	6.502 (2)	14.448 (3)
c, Å	15.911 (4)	15.965 (12)	6.355 (1)
V, Å^3	575.6 (2)	584.4 (6)	1388.7 (8)
d_{measd},[b] g cm^{-1}		1.94	1.68
d_{calcd}, g cm^{-1}	2.019	1.989	1.691
mol formula	$C_9H_2Fe_2O_8$		$C_{15}H_{14}Fe_2O_3$
fw	349.80		353.97
cryst system	hexagonal		orthorhombic
space group	$P6_3$ (No. 173) or $P6_3/m$ (No. 176)[c]		$Pna2_1$ (No. 33) or $Pnma$ (No. 62)[d]
Z	2		4
$F(000)$, electrons	344		720
	Data Collection[e]		
radiation (Mo Kα), Å	0.71069		
mode	ω scan		
scan range	symmetrically over 1.0° about K$\alpha_{1,2}$ maximum		
bkgd	offset 1.0° and −1.0° in ω from K$\alpha_{1,2}$ maximum		
scan rate, deg min^{-1}	4.0		2.0–5.0
check reflctns	4 remeasured after every 96 reflctns (analyses[f] of these data indicated only random fluctuation in intensity during the 10 h required to gather each $Fe_2(CO)_8(\mu\text{-}CH_2)$ data set and the 32 h needed for the $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ data set, with all correction factors less than 0.25σ for $Fe_2(CO)_8(\mu\text{-}CH_2)$ and 0.20σ for $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$)		
2θ range, deg	4.0–70.0		4.0–55.0
total reflctns measd	882	894	1662
data cryst dimens, mm	0.30 × 0.35 × 0.50		0.12 × 0.21 × 0.40
data cryst vol, mm^3	0.036		0.009
data cryst faces	(100), ($\bar{1}00$), (010), ($0\bar{1}0$), (001), ($00\bar{1}$), ($1\bar{1}0$), ($\bar{1}10$), (011), and one minor unidentified face		(010), ($0\bar{1}0$), ($\bar{2}10$), ($2\bar{1}0$), (210), ($\bar{2}\bar{1}0$), ($\bar{2}10$), (011), ($0\bar{1}\bar{1}$), ($01\bar{1}$), ($0\bar{1}1$)
abs coeff, μ(Mo Kα), cm^{-1}	13.1	12.9	21.4
transmission factor	0.70–0.72	0.71–0.73	0.66–0.78

[a] Unit cell parameters were obtained by least-squares refinement of the setting angles of 15 reflections with $32° < 2\theta < 34°$ for $Fe_2(CO)_8(\mu\text{-}CH_2)$ and 45 reflections with $28° < 2\theta < 30°$ for $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$. [b] Flotation at 22 °C in aqueous $ZnCl_2$. [c] Shown by successful refinement to be $P6_3/m$ in this study and in the study of the crystal structure of $Fe_2(CO)_9$.[5] [d] Shown by successful refinement to be $Pnma$ (see text). [e] Syntex P2$_1$ autodiffractometer equipped with a graphite monochromator (bisecting mode) and a Syntex LT-1 inert-gas low-temperature delivery system. [f] Henslee, W. H.; Davis, R. E. *Acta Crystallogr., Sect. B* 1975, *B31*, 1511.

imaginary ($\Delta f''$) corrections[10] for anomalous scattering of Mo Kα radiation were applied to the Fe scattering curve.

$Fe_2(CO)_8(\mu\text{-}CH_2)$ (1). As stated above, least-squares refinements of the two structures (−35 and 22 °C) were begun with the 664 and 611 reflections with $I_o/\sigma(I_o) > 3.0$ for the lower temperature and room-temperature data sets, respectively, with use of the positional parameters obtained[5] for $Fe_2(CO)_9$ in the centric space group $P6_3/m$. (This space group had been previously confirmed[5] as appropriate for the crystal structure of $Fe_2(CO)_9$.) Since there are two molecules of **1** per unit cell, they, like those of the structure of $Fe_2(CO)_9$, occupy sites of C_{3h} ($\bar{3}/m$) symmetry. Hence, the crystal structure of **1** is disordered such that the position of the bridging ligand in the (crystallographic) mirror plane of the molecule is occupied statistically by $^2/_3$ of a CO ligand and $^1/_3$ of a CH_2 ligand. Although the difference in positions of the bridging carbonyl carbon and methylene carbon atoms is too small to be observable, the effects of the statistical reduction of $^1/_3$ of an oxygen atom at the bridging oxygen position, even without accounting for the very small contributions of two $^1/_3$-weight hydrogen atoms, is clearly demonstrated by the least-squares refinement results summarized in Table II.

Table II. Dependence of Crystallographic Least-Squares Refinement on Occupancy of Bridging Oxygen Atom Position[a]

	−35 °C		22 °C	
	$^2/_3$ occup	full occup	$^2/_3$ occup	full occup
	With Isotropic Thermal Parameters			
R[b]	0.102	0.110	0.118	0.126
R_w[b]	0.120	0.132	0.136	0.145
$B_{iso}(O_{br})$, Å^2	3.6 (2)	6.4 (3)	4.4 (3)	8.0 (4)
$B_{iso}(O_{term})$, Å^2	4.0 (1)	4.0 (1)	5.0 (1)	4.9 (1)
	With Anisotropic Thermal Parameters			
R[b]	0.028	0.045	0.029	0.046
R_w[b]	0.034	0.064	0.033	0.060

[a] Hydrogen atom positions were not included in these refinements. Numbers in parentheses are the estimated standard deviations in the least significant digit. [b] R and R_w are defined in the text.

The positions of the methylene hydrogen atoms were then located from a difference Fourier map (at heights of 0.32 and 0.33 e Å^{-3}) in the molecular and crystallographic mirror plane normal to the Fe–Fe bond at $z = {}^1/_4$, with use of the lower temperature data and the atomic parameters obtained from anisotropic refinement of the model containing two bridging carbonyl oxygen atoms per molecule. Although these positions were reasonable (C–H = 0.7 and 0.9 Å, Fe–C–H = 119 and 122°, and H–C–H = 99°) and did refine somewhat satisfactorily, the resulting isotropic thermal parameters were unrealistic (0.6 and 3.0 Å^2) for chemically equivalent atoms, which in view of the disorder is not unexpected. Thus, in the concluding cycles of refinement with both data sets, the hydrogen atoms were held at idealized positions[12] (C–H = 0.95 Å[13] and H–C–H = 109.5°). At

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(11) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(12) Collins, R. C. HIDEAL, a local program which calculates idealized atomic coordinates.

Table III. Fractional Coordinates and Anisotropic Thermal Parameters (× 10^3) for $Fe_2(CO)_8(\mu\text{-}CH_2)^a$

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
				Parameters at −35 °C					
Fe	$^1/_3$	$^2/_3$	0.17134 (2)	200 (1)	β_{11}	133 (1)	$\beta_{11}/2$	0	0
O(1)	0.3310 (7)	1.0865 (5)	$^1/_4$	56 (2)	28 (1)	3 (0)	29 (1)	0	0
O(2)	0.3441 (3)	0.2804 (3)	0.0758 (1)	479 (6)	330 (5)	32 (1)	253 (5)	−13 (2)	−27 (1)
C(1)	0.3308 (5)	0.9097 (4)	$^1/_4$	275 (8)	190 (7)	24 (1)	128 (6)	0	0
C(2)	0.3393 (3)	0.4273 (3)	0.1128 (1)	243 (5)	243 (5)	18 (0)	127 (4)	−4 (1)	−1 (1)
H(1,1)^b	0.1915	0.9242	$^1/_4$	3.6					
H(1,2)^b	0.4687	1.0649	$^1/_4$	3.6					
				Parameters at 22 °C					
Fe	$^1/_3$	$^2/_3$	0.17149 (2)	253 (2)	β_{11}	163 (1)	$\beta_{11}/2$	0	0
O(1)	0.3309 (7)	1.0841 (6)	$^1/_4$	67 (2)	33 (1)	3 (0)	35 (1)	0	0
O(2)	0.3438 (3)	0.2832 (3)	0.0764 (1)	603 (8)	408 (6)	41 (1)	322 (6)	−15 (2)	−34 (2)
C(1)	0.3310 (5)	0.9094 (4)	$^1/_4$	325 (9)	233 (8)	29 (1)	151 (7)	0	0
C(2)	0.3393 (4)	0.4289 (3)	0.1131 (1)	305 (6)	299 (6)	23 (1)	160 (5)	−3 (2)	0 (2)
H(1,1)^b	0.1927	0.9243	$^1/_4$	4.2					
H(1,2)^b	0.4682	1.0639	$^1/_4$	4.2					

[a] See Figure 1 for identity of the atoms. Numbers in parentheses throughout the table are estimated standard deviations in the units of the least significant digits for the corresponding parameter. The expression for the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. For Fe the thermal parameters are given × 10^4. [b] The coordinates of the hydrogen atoms are idealized (see text), and their isotropic thermal parameters (Å^2) are equal to 1.0 Å^2 greater than those of bridging carbon atoms C(1).

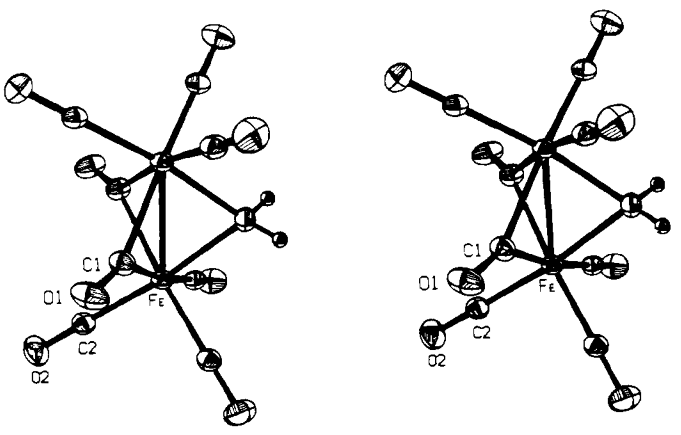

Figure 1. Stereoscopic view of the $Fe_2(CO)_8(\mu\text{-}CH_2)$ molecule (**1**), illustrating the atom numbering scheme. Nonhydrogen atoms are shown as ellipsoids of 30% probability and hydrogen atoms as spheres of radius 0.1 Å.

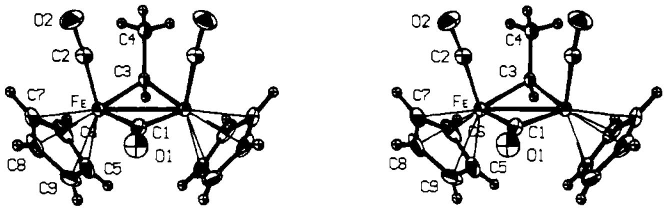

Figure 2. Stereoscopic view of the $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ molecule (**2**), illustrating the atom numbering scheme. Nonhydrogen atoms are shown as ellipsoids of 30% probability and hydrogen atoms as spheres of radius 0.1 Å.

least-squares convergence, $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.027$, $R_w = [\sum w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2} = 0.031$, and a standard deviation of an observation of unit weight $= [\sum w(||F_o| - |F_c||)^2/(m - s)]^{1/2} = 1.77$ for $m = 664$ observations and $s = 34$ variables with the lower temperature data and, in the same order, 0.027, 0.030, and 1.65 for $m = 611$ (and $s = 34$) with the room-temperature data. Structure factor calculations with all reflections measured during data collection (see Table I) gave R and R_w values of 0.042 and 0.034 with the lower temperature data and 0.052 and 0.034 with the room-temperature data. Inspection of each data set after convergence revealed no evidence of secondary extinction.

In the final cycles of refinement, the largest shifts in parameters were less than 0.4 and 0.1 of a corresponding estimated standard deviation (esd) for the lower temperature and room-temperature structures, respectively. The largest peaks on a final difference electron density map, generated with the lower temperature data, were 0.2–0.4 e Å^{-3}.

$[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (2). Full-matrix least-squares convergence was attained, with use of only the 1208 data with $I_o/\sigma(I_o) > 3.0$ for a model in which nonhydrogen atoms were refined anisotropically and hydrogen atoms isotropically, with $R = 0.032$, $R_w = 0.033$, and a standard deviation of an observation of unit weight = 1.87 for $m = 1208$ observations and $s = 127$ variables. Inspection of the data gave no evidence of secondary extinction. A structure factor calculation with all 1662 data measured during data collection gave R and R_w values of 0.050 and 0.035, respectively.

In the final cycle of refinement, shifts in nonhydrogen and hydrogen atomic parameters were less than 0.13 and 0.33 of an esd, respectively. The largest peaks in a final difference electron density map were 0.3–0.6 e Å^{-3}.

Table III presents atomic positional and thermal parameters with corresponding esd's, as obtained from the least-squares inverse matrix, for the room-temperature and lower temperature structures of **1**. The

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(13) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

Table IV. Fractional Coordinates and Anisotropic Thermal Parameters ($\times 10^3$) for Nonhydrogen Atoms of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe[b]	0.10230 (2)	0.16264 (3)	0.18343 (6)	256 (2)	212 (2)	305 (2)	18 (2)	12 (2)	40 (2)
O(1)	0.1851 (4)	$^1/_4$	0.5434 (5)	65 (2)	70 (3)	28 (2)	0	−13 (2)	0
O(2)	−0.0449 (2)	0.1220 (2)	0.4589 (5)	50 (2)	74 (2)	68 (2)	−12 (1)	21 (1)	19 (2)
C(1)	0.1461 (3)	$^1/_4$	0.3823 (7)	32 (2)	39 (2)	28 (2)	0	0 (2)	0
C(2)	0.0123 (2)	0.1409 (2)	0.3471 (5)	38 (2)	32 (2)	42 (2)	−2 (1)	2 (2)	9 (1)
C(3)	0.0346 (3)	$^1/_4$	0.0037 (7)	29 (2)	20 (2)	30 (2)	0	−1 (2)	0
C(4)	−0.0655 (3)	$^1/_4$	−0.0128 (9)	32 (2)	28 (2)	53 (3)	0	−13 (2)	0
C(5)	0.2061 (3)	0.1307 (3)	−0.0313 (7)	62 (3)	34 (2)	64 (3)	19 (2)	34 (2)	8 (2)
C(6)	0.1325 (3)	0.0773 (3)	−0.0780 (7)	76 (3)	58 (3)	52 (2)	39 (2)	−15 (2)	−26 (2)
C(7)	0.1127 (3)	0.0237 (2)	0.0930 (9)	49 (2)	25 (2)	115 (4)	5 (2)	2 (3)	−11 (2)
C(8)	0.1737 (3)	0.0420 (3)	0.2515 (7)	69 (3)	47 (2)	62 (2)	33 (2)	13 (2)	27 (2)
C(9)	0.2322 (2)	0.1081 (3)	0.1748 (8)	28 (2)	55 (2)	80 (3)	13 (2)	−5 (2)	−22 (3)

atom[c]	x	y	z	B[d]	atom[c]	x	y	z	B[d]
H(3)	0.060 (3)	$^1/_4$	−0.138 (7)	3 (1)	H(6)	0.102 (3)	0.077 (3)	−0.203 (8)	8 (1)
H(4A)	−0.094 (3)	$^1/_4$	0.125 (9)	4 (1)	H(7)	0.065 (3)	−0.021 (3)	0.097 (6)	6 (1)
H(4B)	−0.087 (2)	0.302 (2)	−0.086 (5)	3 (2)	H(8)	0.178 (2)	0.017 (3)	0.369 (5)	4 (1)
H(5)	0.238 (3)	0.171 (3)	−0.105 (6)	6 (1)	H(9)	0.273 (3)	0.125 (3)	0.229 (7)	6 (1)

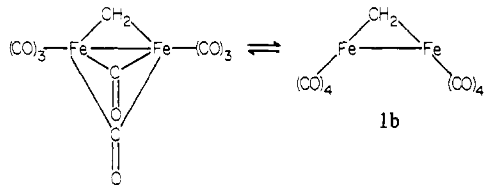
[a] See Figure 2 for identity of the atoms. Numbers in parentheses throughout the table are estimated standard deviations in the units of the least significant digits for the corresponding parameter. The U_{ij} are the mean-square amplitudes of vibration in Å^2 from the general temperature expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] For the Fe atom the anisotropic thermal parameters are given $\times 10^4$. [c] The sequence number of a hydrogen atom corresponds to that of the carbon atom to which it is bound. [d] Isotropic thermal parameters in Å^2.

analogous information for the structure of **2** is given in Table IV. Listings of observed and calculated structure factor amplitudes for all three crystal structures are available.[14]

Discussion

The crystal structures of **1** and **2** consist of discrete molecules with no unusual intermolecular contacts. Figures 1 and 2 offer stereoscopic views of single molecules of **1** and **2**, respectively, and indicate the atom numbering schemes used herein.

Structures of $Fe_2(CO)_8(\mu\text{-}CH_2)$ (1). As communicated previously,[3] in solution **1** is probably an equilibrium mixture of bridging (**1a**) and nonbridging (**1b**) species, in which **1b** is



1a **1b**

apparently the predominant form. In the solid state, however, the structure of $Fe_2(CO)_8(\mu\text{-}CH_2)$ is, as shown in Figure 1, that represented by **1a**. On the other hand, in the crystal structure of $Fe_2(CO)_8(\mu\text{-}C{=}CPh_2)$,[15] all CO ligands are bonded terminally as in **1b**.

Table V provides a listing of bond lengths and angles for both the room-temperature and lower temperature crystal structures of **1**; for ease of comparison the corresponding values for the crystal structure $Fe_2(CO)_9$ are listed also. As is evident from Table V, the two crystal structures of **1** are identical but do differ from that of $Fe_2(CO)_9$ in the lengths of the Fe–Fe and Fe–C(2) bonds. The latter difference may be explained in terms of the increase in π-electron density on the Fe atoms upon replacement of one π-accepting CO ligand by a primarily σ-donating CH_2 ligand. If the carbon atoms of the CH_2 moiety were described as bonded approximately tetrahedrally (sp^3 hybridization) and not trigonally (sp^2 hybridization) (as in $(\eta^5\text{-}C_5H_5)_2Ta(CH_2)(CH_3)$[16] for example), it would have no pπ orbital available to accept electron density from the Fe atoms; hence the π-electron density which would be used in bonding with the nine CO ligands of $Fe_2(CO)_9$ would be distributed to the eight CO ligands of **1**. Now, since the coordination geometry about the Fe atoms—momentarily ignoring the long Fe–Fe bond—is nearly octahedral (see Figure 1 and angles in Table V), bonding with a CO ligand which is trans to the site of substitution, i.e., with a terminal CO ligand, should be preferentially strengthened by this substitution.[17] The crystallographically determined terminal CO positions are the average of one which is trans to the CH_2 position and two which are trans to the bridging CO positions. Hence, a small but perhaps marginally significant decrease

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

	$Fe_2(CO)_8(\mu\text{-}CH_2)$		
	at −35 °C	at 22 °C	$Fe_2(CO)_9$[b]
Fe-Fe′	2.504 (1)	2.507 (1)	2.523 (1)
Fe-C(1)	2.015 (1)	2.022 (1)	2.016 (3)
Fe-C(2)	1.823 (2)	1.822 (2)	1.838 (3)
C(1)-O(1)	1.143 (4)	1.137 (5)	1.176 (5)
C(2)-O(2)	1.131 (2)	1.127 (3)	1.156 (4)
Fe-C(1)-O(1)	141.6 (1)	141.7 (1)	141.2 (1)
Fe-C(2)-O(2)	179.3 (1)	179.3 (2)	177.1 (3)
Fe-Fe′-C(1)	51.6 (1)	51.7 (1)	51.2 (1)
Fe-Fe′-C(2)	120.7 (1)	120.8 (1)	120.9 (1)
C(1)-Fe-C(1)′	85.5 (1)	85.6 (1)	84.9 (1)
C(1)-Fe-C(2)	172.3 (1)	172.4 (1)	172.1 (3)
C(1)-Fe-C(2)′	89.3 (1)	89.3 (1)	89.7 (1)
C(1)-Fe-C(2)′	88.5 (1)	88.4 (1)	88.9 (1)
C(2)-Fe-C(2)′	96.2 (1)	96.2 (1)	96.1 (1)
Fe-C(1)-Fe′	76.6 (1)	76.8 (1)	77.6 (1)
Fe-C(1)-H(1,1)[c]	117	117	
Fe-C(1)-H(1,2)[c]	117	117	

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits. See Figure 1 for identity of the atoms. Coordinates of primed atoms are related to the corresponding coordinates in Table III by a symmetry operation of the space group. [b] Values for the $Fe_2(CO)_9$ structure are taken from ref 5, with distances corrected for the effects of thermal motion. [c] Hydrogen atomic positions are idealized as noted in text.

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(by 0.016 (5) Å) in the lengths of the Fe to (average) terminal CO bonds, but not in the lengths of the Fe to bridging CO bonds, is observed in **1** as an apparent consequence of the substitution of a bridging CH_2 ligand for a bridging CO ligand.

The difference in the lengths of the Fe to bridging CO bonds between the structures of $Fe_2(CO)_9$ and **1** cannot be so satisfactorily interpreted because of disorder. Hence, the structural differences in coordination geometry at the bridging carbonyl and methylene carbon atoms is not observable in this study, although they are in the structure of **2**, as reported below.

The significant shortening (by $\simeq$0.02 Å) of the Fe–Fe distance in **1** compared to that of $Fe_2(CO)_9$ perhaps may be understood by an examination of the molecular orbital description, offered by Lauher et al.,[18] of $Fe_2(CO)_9$. The highest occupied orbitals of $Fe_2(CO)_9$ are e″, which back-bond with carbonyl π* orbitals but which are metal–metal antibonding. However, the fact that these e″ orbitals are strongly metal-bridging carbonyl bonding presumably offsets this antibonding interaction. It may be, then, that in **1** substitution of the CH_2 ligand for a bridging CO ligand lowers the energy of these e″ orbitals to such an extent that they become less metal–metal antibonding, as reflected by this small decrease in the Fe–Fe distance. The Fe–Fe bond in $Fe_2(CO)_8(\mu\text{-}C{=}CPh_2)$,[15] in which there are no bridging CO ligands (and hence no orbitals similar to those in $Fe_2(CO)_9$ to stabilize the antibonding e″ orbitals), is particularly long (2.635 (3) Å) and as such is consistent with these arguments (i.e., that the Fe–Fe bond is strengthened by overlap of the e″ orbitals with orbitals of the bridging ligands). An even more dramatic decrease in metal–metal distance (>0.5 Å) is noted upon comparison of the Ru···Ru separation of the triply methylene-bridged complex $(Me_3P)_6Ru_2(\mu\text{-}CH_2)_3$[1] to the Ru···Ru distances of some triply chlorine-bridged complexes. (A stimulating discussion of the molecular orbital picture of bridged and unbridged dinuclear transition-metal complexes has recently appeared.[19])

Tabulations of the coordination geometries of the structurally characterized unsubstituted and substituted methylene-bridged complexes have been prepared by other authors.[20,21]

Structure of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (2). As noted elsewhere,[7] **2** exhibits rigorous mirror symmetry in which the bridging carbonyl and the substituted methylene group atoms (excluding two related hydrogen atoms) lie in the mirror plane (see Figure 2). Consequently, the cyclopentadienyl rings as well as the terminal carbonyl ligands are necessarily cis. Probably as a consequence of steric interactions, the methyl group of the bridging methylene ligand is directed away from the $\eta^5\text{-}C_5H_5$ rings. The coordination geometry about Fe is pseudotetrahedral, if the center (Cp) of the $\eta^5\text{-}C_5H_5$ ring is regarded as one tetrahedral vertex and the Fe–Fe bond is ignored.

The molecular structure of **2** in this work (see Table VI) and in that communicated by Dyke et al.[7] is in excellent agreement with that reported for the cis (and trans) isomer of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)_2$.[22] There are, in fact, no significant differences between structural features which are common to **2** and this bridging dicarbonyl dimer. The dihedral angle between the planes formed by Fe, Fe′, and C(2) and Fe, Fe′, and C(3) is 166° (164° in the μ-$(CO)_2$ species above), which is consistent with values reported for bridging cis structures and anticipated from results of molecular orbital calculations with *cis*-$[(\eta^5\text{-}C_5H_5)M(CO)_2]_2$ complexes.[23] The length of the metal to bridging methylene carbon bond (Fe–C(3)) is 1.987 (1) Å (cf. 1.986 (3) Å[7]), which is 0.082 Å longer than the Fe to bridging carbonyl distance (Fe–C(1)) but which is consistent with the difference in covalent radii of sp^2 (C(1)) and sp^3 (C(3)) hybridized carbon atoms and in agreement with the distance (1.98 (1) Å) found in $Fe_2(CO)_8(\mu\text{-}C{=}CPh_2)$.[15] The Fe–C(3)–Fe′ angle is 78.9 (1)° (cf. 78.8 (1)°[7]), while that for Fe–C(1)–Fe′ is 83.0 (1)° (cf. 83.0 (1)°[7]). This difference is presumably a result of a compromise between the "formal" hybridization of each carbon atom (sp^3 at C(3), idealized angle = 109.5°; sp^2 at C(1), idealized angle = 120°) and the bonding constraints imposed upon these bridging ligands by the organometallic framework.

Table VI. Bond Lengths (Å) and Bond Angles for $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$[a]

Fe–Fe′	2.525 (1)	C(2)–O(2)	1.152 (4)
Fe–C(1)	1.905 (1)	C(3)–C(4)	1.517 (6)
Fe–C(2)	1.742 (1)	C(5)–C(6)	1.388 (6)
Fe–C(3)	1.987 (1)	C(6)–C(7)	1.367 (7)
Fe–C(5)	2.131 (4)	C(7)–C(8)	1.392 (7)
Fe–C(6)	2.120 (5)	C(8)–C(9)	1.391 (6)
Fe–C(7)	2.094 (4)	C(9)–C(5)	1.407 (7)
Fe–C(8)	2.096 (4)	C(3)–H(3)	0.98 (4)
Fe–C(9)	2.118 (4)	C(4)–H(4A)	0.97 (5)
C(1)–O(1)	1.182 (5)	C(4)–H(4B)	0.94 (3)
C(1)–Fe–Cp[b]	120.5 (1)	Fe–C(3)–C(4)	123.7 (1)
C(2)–Fe–Cp[b]	124.0 (1)	Fe–C(3)–H(3)	109.3 (1)
C(3)–Fe–Cp[b]	123.3 (1)	Fe–C(3)–Fe′	78.9 (1)
Fe′–Fe–Cp[b]	135.4 (1)	H(3)–C(3)–C(4)	108.9 (1)
Fe′–Fe–C(1)	48.5 (1)	C(3)–C(4)–H(4A)	112 (3)
Fe′–Fe–C(2)	100.4 (1)	C(3)–C(4)–H(4B)	112 (2)
Fe′–Fe–C(3)	50.6 (1)	H(4A)–C(4)–H(4B)	107 (2)
C(1)–Fe–C(2)	89.7 (1)	H(4B)–C(4)–H(4B)′	106 (3)
C(1)–Fe–C(3)	98.0 (1)	C(6)–C(5)–C(9)	107.2 (4)
C(2)–Fe–C(3)	93.1 (1)	C(5)–C(6)–C(7)	108.7 (4)
Fe–C(1)–O(1)	138.4 (1)	C(6)–C(7)–C(8)	108.8 (4)
Fe–C(2)–O(2)	176.1 (3)	C(7)–C(8)–C(9)	107.4 (4)
Fe–C(1)–Fe′	83.0 (1)	C(8)–C(9)–C(5)	107.9 (4)

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits. See Figure 2 for identity of the atoms. Coordinates of primed atoms are related to the corresponding coordinates in Table IV by the symmetry operation $x, {}^1/_2 - y, z$. The C–H bond lengths of the C_5H_5 ring are 0.75 (4)–0.97 (4) Å, and the associated H–C–C angles are 119 (3)–133 (3) Å. [b] Cp represents the position of the centroid of the cyclopentadienyl ring.

As shown by molecular orbital calculations,[24] these bridging methylene complexes may be considered as dimetallocyclopropanes electronically. Consistent with this view are the values of the exocyclic R–C–R angles (R = H, alkyl) which fall closer to the tetrahedral value than to those which are generally observed in heterocyclopropanes (114–117°).[25] For example, the H–C–H angle in $H_2Os_3(CO)_{10}(\mu\text{-}CH_2)$ as determined with neutron diffraction data is 106 (1)°.[26] In **2**, the corresponding angle (H(3)–C(3)–C(4)) is 108.9 (1)°. As noted above, details of the coordination geometries of the crystallographically characterized

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moieties have been compiled by other workers.[20]

Finally, it is worthy of mention that the Fe to CO bond lengths decrease with the carbonyl content of the molecules within the series $Fe_2(CO)_9$,[5] $Fe_2(CO)_8(\mu\text{-}CH_2)$ (**1**), $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)_2$,[22] $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**2**). This, of course, is indicative of increasing $d\pi_{Fe} \rightarrow p\pi^*_{CO}$ back-bonding and is in agreement with the established electronic structure of these complexes, in which the η^5-C_5H_5 ligands, principally, and the μ-CRR' ligands lack the electron-acceptor characteristics of CO.[18,23]

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Supplementary Material Available: Listings of observed and calculated structure factors for $Fe_2(CO)_8(\mu\text{-}CH_2)$ at -35 and 22 °C and $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (18 pages). Ordering information is given on any current masthead page.

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Interpretation of σ and π Components in M–P Bonds. Comparison of the Bis(triphenylphosphine) and Bis(triphenyl phosphite) Adducts of Dirhodium Tetraacetate

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The structures of the red bis(triphenyl phosphite) and bis(triphenylphosphine) adducts of dirhodium tetraacetate have been characterized by single-crystal X-ray diffraction studies. The $P(OPh)_3$ adduct crystallizes with monoclinic cell constants $a = 26.134$ (9) Å, $b = 9.951$ (2) Å, $c = 22.512$ (7) Å, and $\beta = 118.55$ (2)°, with four molecules of the complex and four molecules of toluene solvent per unit cell. The structure was solved with the assumption of space group $C2/c$ and refined to conventional R factors: $R(F) = 0.068$ and $R_w(F^2) = 0.075$ for 7073 unique intensities. The PPh_3 adducts forms triclinic crystals with cell constants $a = 9.56$ (1) Å, $b = 9.19$ (1) Å, $c = 12.85$ (1) Å, $\alpha = 110.09$ (5)°, $\beta = 102.56$ (5)°, and $\gamma = 88.85$ (5)°, with one molecule per unit cell, and space group $P\bar{1}$. The structure was solved and refined by full-matrix least-squares to disagreement indices $R(F) = 0.022$ and $R_w(F^2) = 0.075$ for 3557 unique reflections. The dirhodium tetraacetate nucleus in both complexes is essentially identical in structure with that found for the bis(aquo) and bis(pyridine) adducts, except that the Rh–Rh bond is somewhat longer, being 2.4434 (6) Å in the bis($P(OPh)_3$) adduct and 2.4505 (2) Å in the bis(PPh_3) adduct. The Rh–P distances are both extraordinarily long, 2.412 (1) and 2.477 (1) Å, respectively, some 0.1–0.3 Å longer than in normal mononuclear Rh(I) or Rh(III) complexes. As such, any Rh→P π back-bonding is expected to be very much weaker than normal. The results are strongly contrasted against those from a reported comparative study of the $P(OPh)_3$ and PPh_3 complexes of $Cr(CO)_5$, in which π back-bonding effects dominated the M–P bonding. The conclusion is drawn that arguments on the existence of π back-bonding are only valid in limited series of very similar compounds. The structures of the bridged, semibridged, and nonbridged dirhodium complexes $Rh_2(OAc)_4(PPh_3)_2$, $Rh_2(OAc)_2(dmg)_2(PPh_3)_2$, and $Rh_2(dmg)_4(PPh_3)_2$ are briefly compared.

Introduction

The intimate interactions between the metal atoms in cluster complexes permit the electronic influence of various ligands to be both dramatic and pervasive, in the sense that "these can be transmitted through the cluster from one metal atom to another."[1] Thus the mutual interactions of metal–metal and metal–ligand bonds portend to be an extremely important aspect of the versatile and growing chemistry of cluster-based systems. We have consequently undertaken a systematic, high-precision structural study of an extended homologous series of dinuclear rhodium complexes in the expectation that an understanding of substituent effects on the metal–metal interactions in clusters will be best achieved by first understanding the cumulative bonding effects in the smallest of metal cluster compounds.

We have chosen the dirhodium tetraacetate nucleus for these studies for four primary reasons. First, the metal–metal bond is unusually short[2] and, by implication, quite strong, thus assuring the ready transmission of electronic substituent effects. Second, it has proven possible to prepare a wide variety of axial ligand adducts of this nucleus,[3] thereby availing us the opportunity to probe the Rh–Rh bond with a broad range of ligand strengths. Third, the essentially octahedral coordination of the rhodium atoms yields a very stable configuration of the bridging acetate groups. This leaves the axial sites extraordinarily unrestricted and presumably would even permit axial ligands with cone angles[4] as great as 180° to be accommodated without steric difficulty. Fourth, the Rh–Rh bond in the tetracarboxylate complexes has been described as both triple[2,5] and as single[6,7] by different research groups, and we hoped by our studies to contribute to a resolution of the question of the character of the metal–metal bond in this system. This

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