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Infrared Spectrum of Hexacarbonylbis(μ-carbonyl)(μ-methylene)diiron, $Fe_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}CH_2)$, in Cryogenic Matrices

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The Fourier transform infrared spectrum of hexacarbonylbis(μ-carbonyl)(μ-methylene)diiron, $Fe_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}CH_2)$, has been measured in argon and nitrogen matrices. The vibrational spectrum of the Fe_2CH_2 moiety has also been identified. Vibrational mode assignments of the methylene ligand have been verified with use of carbon-13- and deuterium-labeled compounds. With use of a triatomic approximation the CH_2 bond angle has been estimated to be 106° on the basis of the methylene CH_2 symmetric and asymmetric stretching frequencies. This is indicative of an sp^3 hybridization around the carbon atom. Carbon-13 NMR studies gave a value of $\delta = 89.75$ ($J_{C-H} = 147$ Hz) for the methylene carbon.

Introduction

The CH_2 fragment bonded to one or more metal centers is of fundamental importance to organometallic chemistry and catalysis.[1,2] Methylene groups have been observed to bond in a terminal fashion to metal atoms[3-5] or in a μ-bridging fashion in multimetal centers[6-25] for several well-characterized discrete molecular systems. In the latter case, the methylene units have been shown to exhibit fluxional behavior in a bridge $\rightleftarrows$ terminal equilibrium by NMR spectroscopy.[6,21,25] The infrared spectra of these compounds are of importance in helping to identify these species as intermediates in heterogeneous catalytic systems where more definitive structural analysis may be lacking. A number of methylene complexes have been studied by X-ray photoelectron spectroscopy;[26] however, vibrational spectroscopy for complexes of this type is scarce. Some of us recently reported the isolation of iron methylene, $FeCH_2$, and possibly diiron methylene, Fe_2CH_2, when Fe atoms were cocondensed with CH_2N_2 in an argon matrix.[27] For purposes of comparison to these unligated metal systems, we have undertaken the study of the vibbrational spectra of $Fe_2(CO)_8(\mu\text{-}CH_2)$, $Fe_2(CO)_8(\mu\text{-}^{13}CH_2)$, and $Fe_2(CO)_8(\mu\text{-}CD_2)$ by conventional and matrix isolation techniques.

Experimental Section

The syntheses of the $Fe_2(CO)_8(\mu\text{-}CH_2)$, $Fe_2(CO)_8(\mu\text{-}^{13}CH_2)$, and $Fe_2(CO)_8(\mu\text{-}CD_2)$ complexes were carried out with use of standard Schlenk techniques by the method of Pettit.[28,29] CD_2I_2 and $^{13}CH_2I_2$ were obtained from Merck Isotopes, Ltd. The product was sublimed (10^{-5} Torr, hot H_2O bath, 45–55 °C), but no differences in spectra were observed between that compound and material obtained directly from the synthesis without further purification. KBr spectra were measured on a Perkin-Elmer 1430 ratio recording spectrometer.

A complete description of the multisurface matrix isolation apparatus has been published.[30] For a typical experiment, the sample was sublimed at 45 °C and cocondensed with argon (Matheson, 99.9998%) or nitrogen (Matheson, 99.9995%) onto a rhodium-plated copper surface cooled to 12 K with a closed-cycle helium refrigerator (Air Products Displex, CSW-202). The molar ratio of the sample to the matrix gas was about 1:150, as determined by a quartz crystal microbalance mounted on the matrix block. After a 30-min deposition, the infrared spectra of the matrix-isolated species were measured with an IBM IR-98 Fourier-transform infrared vacuum spectrometer. The frequencies were measured over the range 4000–300 cm^{-1} and to an accuracy of ± 0.05 cm^{-1}. Infrared spectra of KBr disks of the same sample were also recorded at room temperature. ^{13}C NMR spectra of $Fe_2(CO)_8(\mu\text{-}^{13}CH_2)$ in toluene-d_8 solution were also measured with an IBM AF300 Fourier-transform nuclear magnetic resonance spectrometer.

Results

Figure 1 shows the infrared spectra corresponding to the μ-bridging CH_2 vibrations of $Fe_2(CO)_8(\mu\text{-}CH_2)$ in argon (Figure 1A) and nitrogen (Figure 1B) matrices and in a KBr disk (Figure 1C). The splitting of bands observed in an Ar matrix may be due to matrix site effects or molecular distortion.[31] Frequencies measured at 2933.2 and 2981.2 cm^{-1} in a nitrogen matrix were assigned to the symmetric and asymmetric CH_2 stretching modes; the corresponding bands were measured in an Ar matrix at 2925.0 and 2975.6 cm^{-1} and in a KBr disk at 2915.9 and 2963.1 cm^{-1}, respectively. The CH_2 wagging mode was measured at 974.4 cm^{-1} (N_2), 978.0 cm^{-1} (Ar), and 963.8 cm^{-1} (KBr). A weak absorption at 1379.3 cm^{-1} was measured in a KBr disk and was assigned to the symmetric bending mode of the CH_2 group; however, the corresponding absorption band was not detected in either argon or nitrogen matrices. The bands at 759.8 cm^{-1} (Ar), 758.4 cm^{-1} (N_2), and 764.6 cm^{-1} (KBr) were assigned to the CH_2 rocking mode. Weak features appeared at 936.5 and 932.8 cm^{-1} in argon and nitrogen matrices, respectively. A possible assignment for these absorptions would be the CH_2 twisting mode, normally IR

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(1) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.
(2) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.
(3) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.
(4) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804.
(5) Fischer, H.; Weber, L. *Chem. Ber.* **1984**, *117*, 3340.
(6) Holmgren, J. S.; Shapley, J. R. *Organometallics* **1985**, *4*, 793.
(7) Shapley, J. R.; Sievert, A. C.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 6975.
(8) Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1278.
(9) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 825.
(10) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1979**, *99*, 5225.
(11) Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J.; Seddon, K. R. *J. Chem. Soc., Chem. Commun.* **1978**, 749.
(12) Murray, H. H.; Fackler, J. P., Jr.; Mazany, A. M. *Organometallics* **1984**, *3*, 1310.
(13) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134.
(14) Clemente, D. A.; Biagini, M. C.; Rees, B.; Herrmann, W. A. *Inorg. Chem.* **1982**, *21*, 3741.
(15) Gadol, S. M.; Davis, R. E. *Organometallics* **1982**, *1*, 1607.
(16) Green, M.; Hankey, D. R.; Murray, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1981**, 689.
(17) Herrmann, W. A.; Huggins, J. M.; Bauer, C.; Smischek, M.; Pfisterer, H.; Ziegler, M. L. *J. Organomet. Chem.* **1982**, *226*, C59.
(18) Herrmann, W. A.; Reiter, B.; Biersack, H. *J. Organomet. Chem.* **1975**, *97*, 245.
(19) Hursthouse, M. B.; Jones, R. A.; Malik, K. M. A.; Wilkinson, G. *J. Am. Chem. Soc.* **1979**, *101*, 4128.
(20) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911.
(21) Laws, W. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1020.
(22) Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679.
(23) Nutton, A.; Vazquez, de Miguel, A.; Isobe, K.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1983**, 166.
(24) Wright, M. E.; Nelson, G. O. *J. Organomet. Chem.* **1984**, *263*, 371.
(25) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 464.
(26) Xiang, S. F.; Chen, H. W.; Eyermann, C. J.; Jolly, W. L.; Smit, S. P.; Theopold, K. H.; Bergman, R. G.; Herrmann, W. A.; Pettit, R. *Organometallics* **1982**, *1*, 1200.
(27) Chang, S.-C.; Kafafi, Z. H.; Hauge, R. H.; Billups, W. E.; Margrave, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 1447.
(28) Sumner, C. E., Jr.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 1752.
(29) Sumner, C. E., Jr.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350.
(30) Hauge, R. H.; Fredin, L.; Kafafi, Z. H.; Margrave, J. L. *Appl. Spectrosc.* **1986**, *40*, 588.
(31) Poliakoff, M.; Turner, J. J. *J. Chem. Soc. A* **1971**, 654.

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Table II. FTIR Frequencies (cm^{-1}) of the Fe_2CH_2 Moiety of Hexacarbonylbis(μ-carbonyl)(μ-methylene)diiron Measured in Argon and in Nitrogen Matrices and in a Potassium Bromide Disk

	$Fe_2(CO)_3(\mu\text{-}CH_2)$			$Fe_2(CO)_8(\mu\text{-}CD_2)$			$Fe_2(CO)_8(\mu\text{-}^{13}CH_2)$		
vibrational mode	Ar	N_2	KBr	Ar	N_2	KBr	Ar	N_2	KBr
ν_1 CH_2 sym str	2925.0	2933.2	2915.9	2152.9	2157.2	2146.9	2919.0	2926.5	2910.1
ν_3 CH_2 scissor			1379.3			1025.7			1372.8
ν_4 Fe–C str	646.5	646.3		543.8	545.0		626.0	626.8	
ν_5 CH_2 twist	936.5	932.8		723.7	725.0		933.1	928.1	
ν_6 CH_2 wag	978.0	974.4	963.8	754.5	752.1	747.8	973.6	970.5	959.9
ν_8 CH_2 asym str	2975.6	2981.2	2963.1	2235.8	2243.5	2228.1	2964.5	2971.3	2950.8
ν_9 CH_2 rock	759.8	758.4	764.6	627.7	626.8		753.6	753.1	759.6

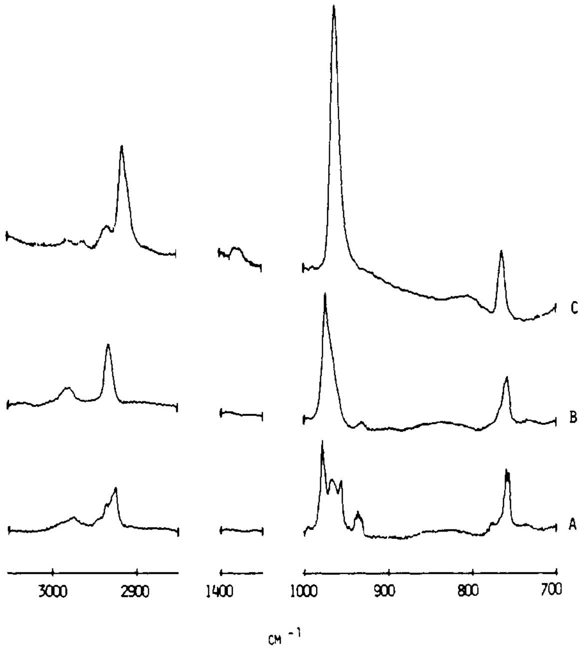

Figure 1. CH_2 stretching and deformation regions of $Fe_2(CO)_8(\mu\text{-}CH_2)$ in argon (A) and nitrogen (B) matrices and in a KBr disk (C). The strongest peak has an absorbance of 0.31.

inactive for C_{2v} symmetry. A similar corresponding absorption was not observed in a KBr disk.

Portions of the infrared spectra corresponding to the μ-bridging methylene vibrations of $Fe_2(CO)_8(\mu\text{-}CH_2)$ (Figure 2A), $Fe_2(CO)_8(\mu\text{-}^{13}CH_2)$ (Figure 2B), and $Fe_2(CO)_8(\mu\text{-}CD_2)$ (Figure 2C) in nitrogen matrices are given in Table II. All the measured frequencies underwent carbon-13 and deuterium shifts as expected for a bridged methylene group.

Figure 3 shows the infrared spectra of the 700–250-cm^{-1} region of $Fe_2(CO)_8(\mu\text{-}CH_2)$ (Figure 3A), $Fe_2(CO)_8(\mu\text{-}^{13}CH_2)$ (Figure 3B), and $Fe_2(CO'_8(\mu\text{-}CD_2)$ (Figure 3C) in argon matrices. The absorptions in the 650–500-cm^{-1} region are related to the carbonyl deformation modes and will not be discussed in this paper. Below 500 cm^{-1}, two weak bands appeared at 392.0 and 352.9 cm^{-1} (Figure 3A) and did not show any isotopic shift for either $Fe_2(CO)_8(\mu\text{-}^{13}CH_2)$ (Figure 3B) or $Fe_2(CO)_8(\mu\text{-}CD_2)$ (Figure 3C) and thus were assigned to terminal and bridging metal–carbonyl stretching modes.[32] The metal–methylene stretching frequencies were difficult to locate. The spectrum of the deuterium-labeled compound (Figure 3C) indicated significant interactions between the carbonyl deformation modes and the methylene vibration modes. However, carbon-13 substitution of the μ-CH_2 group helped identify the frequencies of the metal–carbon stretching mode as 646.5 and 626.0 cm^{-1} for $Fe_2(CO)_8(\mu\text{-}CH_2)$ (Figure 3A) and $Fe_2(CO)_8(\mu\text{-}^{13}CH_2)$ (Figure 3B), respectively. The corresponding band appeared at 543.8 cm^{-1} for $Fe_2(CO)_8(\mu_2CD_2)$ (Figure 3C).

Figure 4 shows the spectra of the CO stretching and deformation modes of $Fe_2(CO)_8(\mu\text{-}CH_2)$ in argon (Figure 4A) and

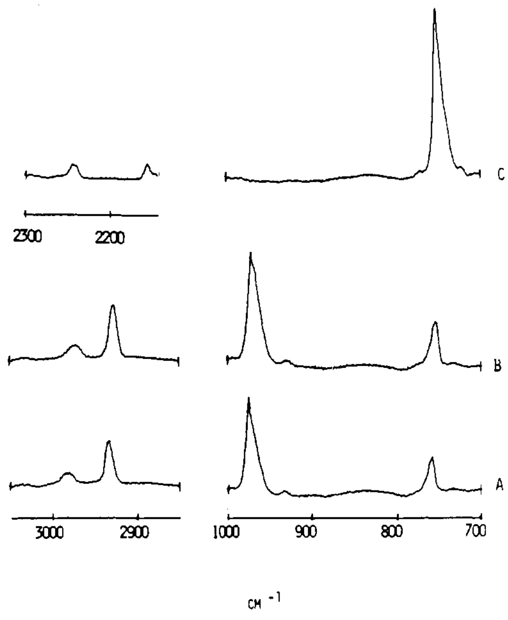

Figure 2. CH_2 stretching and deformation regions of $Fe_2(CO)_8(\mu\text{-}CH_2)$ (A), $Fe_2(CO)_8(\mu\text{-}^{13}CH_2)$ (B), and $Fe_2(CO)_8(\mu\text{-}CD_2)$ (C) in nitrogen matrices. The strongest peak has an absorbance of 1.44.

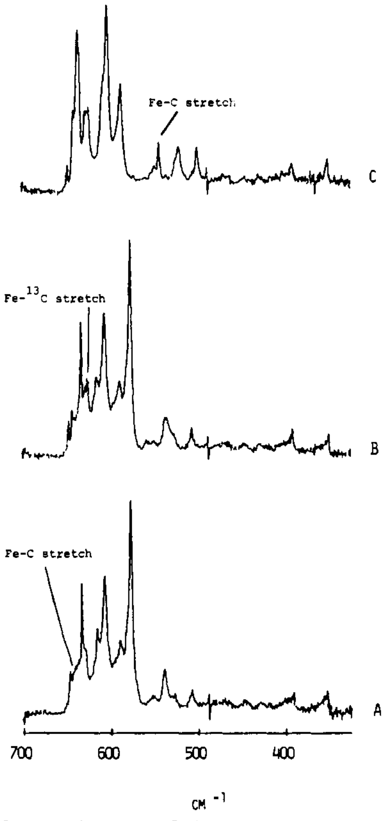

Figure 3. Fe–C stretching and CO deformation regions of $Fe_2(CO)_8(\mu\text{-}CH_2)$ (A), $Fe_2(CO)_8(\mu\text{-}^{13}CH_2)$ (B), and $Fe_2(CO)_8(\mu\text{-}CD_2)$ (C) in argon matrices. The strongest peak has an absorbance of 0.80.

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(32) Oxton, I. A. *J. Mol. Struct.* **1982**, *78*, 77.

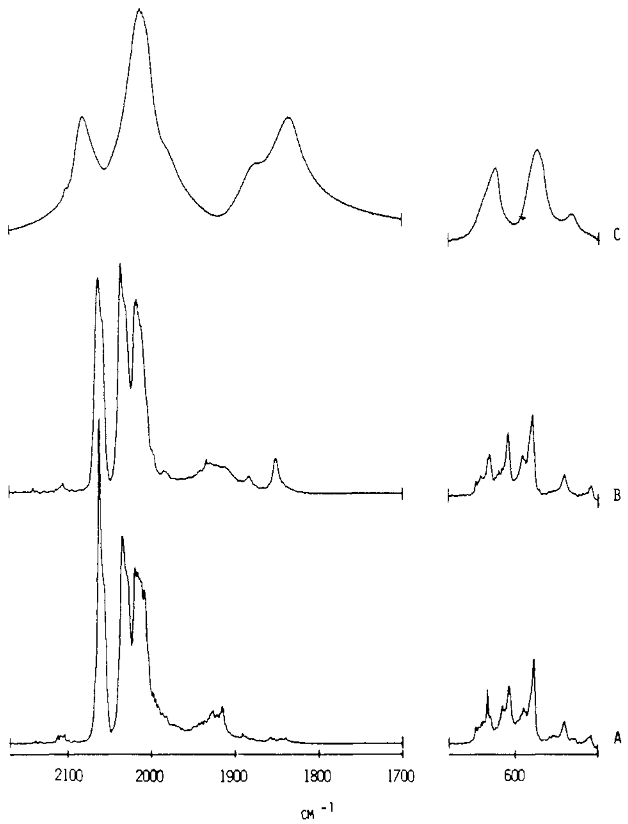
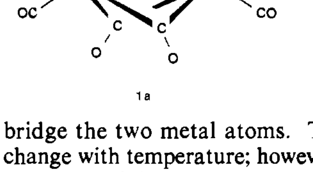


Figure 4. CO stretching and deformation regions of $Fe_2(CO)_8(\mu\text{-}CH_2)$ in argon (A) and nitrogen (B) matrices and in a KBr disk (C). The strongest peak has an absorbance of 3.00.

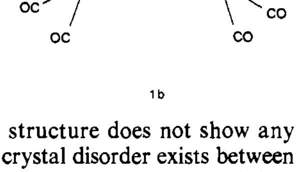
nitrogen (Figure 4B) matrices and in a KBr disk (Figure 4C). Although the patterns and intensity of the spectrum in a KBr disk are different from those in cryogenic matrices, all the terminal CO stretching frequencies appeared above 2000 cm^{-1} in all of the three different environments. The bridging CO stretching absorption band in an argon matrix was weak compared to the same absorption in a nitrogen matrix and in a KBr disk. Since the infrared spectra of Figure 3 showed two different metal carbonyl stretches indicative of the presence of both terminal and bridged carbonyls, it seems unlikely that the structure of $Fe_2(CO)_8(\mu\text{-}CH_2)$ will be different in argon matrices. All the measured frequencies of CO vibrations for $Fe_2(CO)_8(\mu\text{-}CH_2)$, $Fe_2(CO)_8(\mu\text{-}^{13}CH_2)$, and $Fe_2(CO)_8(\mu\text{-}CD_2)$ in argon and nitrogen matrices and in a KBr disk are given in Table I (supplementary material).

Discussion

$Fe_2(CO)_8(\mu\text{-}CH_2)$, more accurately described as $Fe_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}CH_2)$, first synthesized by Pettit's group,[28,29] is a thoroughly characterized organometallic cluster compound. The crystal structure of $Fe_2(CO)_8(\mu\text{-}CH_2)$ has been determined[28,33] at −35 and 22 °C as shown in **1a**, where two of the CO ligands



1a



1b

bridge the two metal atoms. The structure does not show any change with temperature; however, crystal disorder exists between the two bridging carbonyls and the bridging CH_2 unit and does not allow determination of bond parameters for the methylene group. In this respect, the molecular geometry is isostructural with that of $Fe_2(CO)_9$ with a C_{3h} ($\bar{6}$) symmetry. In solutions, the molecule exists as an equilibrium mixture of forms **1a** and **1b** with the predominant isomer being that of the unbridged carbonyl ligands. These conclusions were deduced from the infrared spectra of this organometallic complex in CH_2Cl_2, benzene or hexane, which exhibited only terminal CO stretching absorptions. The infrared spectrum of $Fe_2(CO)_8(\mu\text{-}CH_2)$ isolated in solid nitrogen indicates the presence of both terminal and bridged carbonyl ligands. This is reflected in the C–O as well as in the Fe–CO stretching regions, where the frequencies of the terminal CO's are higher than those of their bridged analogues. In argon matrices, the absorption bands associated with the bridged CO stretching modes were very weak compared to those in nitrogen matrices and in KBr disks; however, the band due to the Fe–CO stretching mode associated with the bridged CO was observed. Since the extinction coefficients of stretching absorptions due to bridging carbonyl groups have been reported[31] to be extremely sensitive to environments, and the rest of the spectrum of $Fe_2(CO)_8(\mu\text{-}CH_2)$ in an argon matrix is very similar to the spectrum in a nitrogen matrix or in a KBr disk, the structure of this molecule in all matrices is thought to be the same as the crystal structure, namely the CO-bridged form of **1a**.

The vibrational spectrum due to the carbonyl ligands present in hexacarbonylbis(μ-carbonyl)(μ-methylene)diiron will not be analyzed in this paper. Attention, rather, will be focused on the (μ-methylene)diiron vibrational spectrum along with its carbon-13 and deuterium isotopic shifts. The local symmetry of the $FeCH_2Fe$ group can be treated as C_{2v}. Nine vibrational modes are expected from such a molecular system with the group representation

$$\Gamma_{vib} = 4A_1 + A_2 + 2B_1 + 2B_2$$

IR frequencies of $FeCH_2Fe$, $Fe^{13}CH_2Fe$, and $FeCD_2Fe$ measured in argon and nitrogen matrices and in KBr disks are listed in Table II. The assignment of the totally symmetric vibrational modes was based on the Redlich–Teller product rule using carbon-13 and deuterium isotope labeled frequencies. The frequencies of the symmetric CH_2 bending mode used in these calculations were those measured in KBr disks. No frequency assignable to the iron–iron stretching mode could be observed. This absorption is expected to lie around 260 cm^{-1}.[34] The other frequency located in the carbon–hydrogen stretching region was assigned to the asymmetric stretching mode. Three frequencies at 978.0, 936.5, and 759.8 cm^{-1} in Ar were measured in the CH_2 deformation region. The 978.0-cm^{-1} absorption was quite intense and is typical of that of the CH_2 wagging mode. The weaker feature at 759.8 cm^{-1} was assigned to the CH_2 rocking mode on the basis of its intensity and by comparison to its counterpart in other organometallic complexes that have a bridged methylene group (see Table III). Finally there remains a fairly weak absorption at 936.5 cm^{-1} whose presence is unexpected. This frequency has been assigned to the CH_2 twist mode, which is normally infrared-inactive for a molecule of C_{2v} symmetry. The lowering of the molecular symmetry in cryogenic matrices either by molecular distortion or by low site symmetry is possible. The activation of this mode for the compounds $Os_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}CH_2)$ and $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ has been observed.[35] Neutron diffraction studies carried out on $Os_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}CH_2)$ have shown[36] that the methylene carbon atom has a distorted-tetrahedral geometry with an Os–C–Os angle of 82.1° and an H–C–H angle of 106.0°.

The frequencies measured for the bridged methylene in $Fe_2(CO)_8(\mu\text{-}CH_2)$ and in other organic and organometallic compounds are compared in Table III. It is interesting that there is a fairly good agreement between these values, especially those measured in similar organometallic cluster compounds.

The CH_2 bond angle was estimated on the basis of the triatomic molecule approximation for the carbon–hydrogen stretching and the CH_2 bending frequencies[37,38] of Fe_2CH_2, $Fe_2{}^{13}CH_2$, and

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(33) Meyer, B. B.; Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1981**, *20*, 3024.

(34) Butler, I. S.; Kishner, S.; Plowman, K. R. *J. Mol. Struct.* **1978**, *43*, 9.

(35) Oxton, I. A.; Powell, D. B.; Sheppard, N.; Burgess, K.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1982**, 719.

(36) Schultz, A. J.; Williams, J. M.; Calvert, R. B.; Shapley, J. R.; Stucky, G. D. *Inorg. Chem.* **1979**, *18*, 319.

Table III. Comparison between the Frequencies ν (cm^{-1}) of the Bridged CH_2 Group in $Fe_2(CO)_8(\mu\text{-}CH_2)$ and in Other Organometallic and Organic Compounds

vibrational mode	CH_2 / \ Fe–Fe present work	CH_2 / \ Os–Os ref 35		CH_2 / \ Ru–Ru ref 6	CH_2 / \ C=C ref 40	CH_2 / \ N=N ref 41
ν_1 CH_2 sym str	2925.0	2935[a]	2949[b]	2942	2909	3020
ν_3 CH_2 scissor	(1379.3)[c]	1428	1426	1390	1483	1458
ν_4 M–C str	646.5	660			905[d]	991[e]
ν_5 CH_2 twist	936.5	869	850		(996)[f]	(971)[f]
ν_6 CH_2 wag	978.0	961	974	972	1011	967
ν_8 CH_2 asym str	2975.6	2984	2990	2990	2995	3131
ν_9 CH_2 rock	759.8	811	796	775	1088	1125

[a] $Os_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}CH_2)$. [b] $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$. [c] Measured in a KBr disk. [d] C–C symmetric stretch. [e] N–C symmetric stretch. [f] Estimated values.

Table IV. Structural Data for μ-Methylene Organometallic Cluster Compounds

compds	R_{M-M}, pm	M–C–M, deg	H–C–H, deg	ref
$(\mu\text{-}CH_2)(\mu\text{-}CO)_2Fe_2(CO)_6$	250.4	76.8	106	33, present work
$(\mu\text{-}CH_2)_3Ru_2(P(CH_3)_3)_2$	264.3	77.3	107	39
$(\mu\text{-}CH_2)(\mu\text{-}H)_2Os_3(CO)_{10}$	282.4	82.1	106.0[a]	36, 42
$(\mu\text{-}CH_2)(\mu\text{-}CO)(Cp)(CO)FeMn(CO)_4$	261.8	81.4	110	44
$(\mu\text{-}CH_2)Mn_2(\eta^5\text{-}C_5H_5)_2(CO)_4$	279.9	87.4	109	39
$(\mu\text{-}CH_2)Mn_2(\eta^5\text{-}CH_3C_5H_4)_2(CO)_4$	277.9	87.3	92	43
$(\mu\text{-}CH_2)Co_2(\eta^5\text{-}CH_3C_5H_4)_2(CO)_2$	249.7	81.0	108	25
$(\mu\text{-}CH_2)Rh_2(\eta^5\text{-}C_5H_5)_2(CO)_2$	266.2	81.0	110.4[a]	39

[a] Neutron diffraction study.

Fe_2CD_2, respectively. A value of 106° was calculated, which coincides with that obtained for the bridged methylene in $Os_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}CH_2)$ from the neutron diffraction study.[36] Another neutron diffraction measurement gave[39] an H–C–H bond angle of 110.4° for μ-CH_2 in $Rh_2(Cp)_2(CO)_2(\mu\text{-}CH_2)$. Thus, the methylene carbon atom is best described in terms of sp^3 hybridization. This is further supported from the carbon-13 NMR study carried out on $Fe_2(CO)_8(\mu\text{-}^{13}CH_2)$, which showed the methylene carbon signal at $\delta = 89.75$ with $J_{C-H} = 147$ Hz, very close to the value of 146 Hz measured for $Rh_2(Cp)_2(CO)_2(\mu\text{-}CH_2)$.[44] Table IV lists some structural parameters for different organometallic cluster compounds containing a μ-CH_2 group. The metal–metal bond length is quite short in this class of μ-methylene transition-metal complexes and varies between 2.5 and 2.8 Å. The metal–metal interactions are necessary to provide enhanced stability to the methylene bridging. The M–C–M angle around the methylene carbon atom is generally very acute and shows little variation with the nature of the metals involved. Typically, the angles fall in the range 76–87°. The H–C–H bond angle is close to a tetrahedral value in most cases; however, the only two previously determined reliable values listed in Table IV are those obtained from the neutron diffraction studies.[36,39,42]

Concluding Remarks

1. The FTIR spectrum of matrix-isolated $Fe_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}CH_2)$ has been measured in solid argon and nitrogen.
2. Carbon-13 and deuterium isotopic shifts have been measured for $Fe_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}^{13}CH_2)$ and $Fe_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}CD_2)$, respectively.
3. An H–C–H bond angle of 106° was calculated on the basis of the triatomic molecule approximation using the carbon–hydrogen stretching and the CH_2 bending frequencies of μ-CH_2, μ-$^{13}CH_2$, and μ-CD_2, respectively.
4. A coupling constant of 147 Hz is seen in the carbon-13 NMR spectrum. This is close to the value of $Rh_2(Cp)_2(CO)_2(\mu\text{-}CH_2)$, for which neutron diffraction analysis gives an H–C–H bond angle of 110.4°, indicating an sp^3 hybridization around the bridged methylene carbon.

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Supplementary Material Available: A complete listing of frequencies associated with the carbonyl ligands as seen in argon and nitrogen matrices and in KBr pellets (Table I) (2 pages). Ordering information is given on any current masthead page.

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(37) Allavena, M.; Rysnik, R.; White, D.; Calder, V.; Mann, E. *J. Chem. Phys.* **1969**, *50*, 3399.
(38) Green, D. W.; Ervin, K. M. *J. Mol. Spectrosc.* **1981**, *88*, 51.
(39) Takusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Hermann, W. A. *Inorg. Chem.* **1981**, *20*, 3060.
(40) Wiberg, K. B.; Dempsey, R. C.; Wendoloski, J. J. *J. Phys. Chem.***1984**, *88*, 5596.
(41) Ettinger, R. *J. Chem. Phys.* **1964**, *740*, 1693.
(42) Calvert, R. B.; Shapley, J. R.; Schultz, A. J.; Williams, J. M.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6240.
(43) Greswick, M.; Bernal, I.; Reiter, A. B.; Herrmann, W. A. *Inorg. Chem.* **1982**, *21*, 645.
(44) Herrmann, W. A.; Plank, J.; Riedel, D.; Ziegler, M. L.; Weidenhammer, K.; Guggolz, E.; Balbach, B. *J. Am. Chem. Soc.* **1981**, *103*, 63.