for this study. We also thank Dr. George Rouschias for providing the sample of the complex.

Registry No. $[Ir(CNMe)(diphos)_2]ClO_4$, 40226-65-1.

Supplementary Material Available: Tables of the observed and calculated structure factor amplitudes, and of the parameters used in calculating the hydrogen atom contributions to the F_c, 40 pages. Ordering information is given on any current masthead page.

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Structural and Carbon-13 Nuclear Resonance Studies of a Compound Containing the $Fe_2(CO)_6$ Entity. Hexacarbonyl[μ-(1,2,5-η:1,4,5-η)-3-oxo-1,2,4,5-tetraphenyl-1,4-pentadiene-1,5-diyl]diiron(*Fe–Fe*)

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Diphenylacetylene reacts with diiron nonacarbonyl in tetrahydrofuran to produce a compound of empirical formula $Fe_2(CO)_7(PhCCPh)_2$, identical with a product obtained some years ago by W. Hübel and coworkers. An x-ray crystallographic study has shown that the compound consists of an $(OC)_3Fe–Fe(CO)_3$ unit to which is bonded $-CPh{=}CPhC(O)CPh{=}CPh-$ in such a way that each terminal carbon atom forms a σ bond to one iron atom while the π bond in which it is involved forms a donor bond to the other iron atom. The entire structure then possesses only one symmetry element, a twofold axis of symmetry passing through the CO group of the ligand and bisecting the Fe–Fe bond. The three CO groups on each iron atom are nonequivalent. The structure is analogous to that previously determined by Piron, Piret, Meunier-Piret, and van Meersche for the tetramethyl compound. The Fe–Fe distance is 2.536 (1) Å. Crystal data: space group $P2_1/n$; $a = 13.167$ (5), $b = 11.535$ (3), $c = 21.787$ (8) Å; $\beta = 95.11$ (2)°; $Z = 4$. The ^{13}C NMR spectrum was recorded at various temperatures from -25 to $+85°$. At the lowest temperatures three separate, equally intense, equally narrow signals are observed, in accord with the molecular structure. These begin to broaden at about $-10°$ and coalesce at about $+30°$ to a single broad resonance which sharpens as the temperature is raised further. There is no indication of preferential collapse of any two signals. From line shape analysis, the activation parameters for carbonyl scrambling have been estimated to be $\Delta G^{\ddagger}(300\ K) = 15.1$ (2) kcal mol^{-1}, $\Delta H^{\ddagger} = 14.1$ (1) kcal mol^{-1}, $\Delta S^{\ddagger} = -3.2$ (5) cal mol^{-1} deg^{-1}, $E_a = 14.7$ (2) kcal mol^{-1}, and $A = 3.4$ (8) $\times 10^{12}$ sec^{-1}.

Introduction

Let us begin by indicating the context of the work reported here, which is but one small contribution to a very large field. There exists a vast number of dinuclear metal carbonyls of the type **1**. The two characteristic features are (1) the presence of terminal CO groups, on both metal atoms, and (2) the existence of a single bond between the metal atoms. The variable features are (1) the identity of the metal atoms, which may be identical or different, (2) the number of CO groups on each metal atom, which can range from 1 to 5 and may be the same or different for the two metal atoms when the metal atoms are different or even when they are the same, (3) the nature of L and L' which may themselves be CO groups, which may be bridging groups such as RS, S_2, R_2P, R_2N, R_2Ge, $RC{\equiv}CR$, etc., which may be polyene or polyenyl groups, or which may be different regions of one large polyene

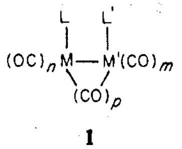

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

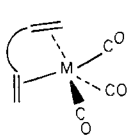
Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe1	0.58045 (7)	0.06328 (7)	0.26511 (4)	0.00491 (5)	0.00479 (6)	0.00207 (2)	0.0002 (1)	0.00038 (6)	−0.00003 (6)
Fe2	0.41025 (7)	0.16749 (8)	0.25228 (4)	0.00418 (5)	0.00547 (6)	0.00228 (2)	−0.0006 (1)	0.00079 (5)	−0.00044 (6)
O1	0.7850 (4)	0.1098 (5)	0.3237 (3)	0.0057 (3)	0.0115 (5)	0.0046 (2)	0.0001 (7)	−0.0025 (4)	−0.0018 (5)
O2	0.6326 (4)	−0.1420 (4)	0.1932 (3)	0.0098 (4)	0.0089 (4)	0.0043 (2)	0.0045 (7)	0.0010 (4)	−0.0053 (4)
O3	0.5151 (5)	−0.1060 (4)	0.3537 (3)	0.0153 (6)	0.0067 (4)	0.0037 (1)	−0.0007 (8)	0.0047 (5)	0.0029 (4)
O4	0.2657 (4)	0.2170 (5)	0.3459 (2)	0.0073 (3)	0.0134 (5)	0.0037 (1)	−0.0003 (8)	0.0045 (3)	−0.0024 (5)
O5	0.3112 (4)	0.3243 (5)	0.1596 (2)	0.0079 (4)	0.0110 (5)	0.0037 (1)	0.0045 (7)	0.0007 (4)	0.0033 (4)
O6	0.2993 (4)	−0.0525 (4)	0.2394 (3)	0.0084 (4)	0.0084 (4)	0.0044 (2)	−0.0067 (7)	0.0022 (4)	−0.0009 (4)
O7	0.6619 (3)	0.3760 (4)	0.2300 (2)	0.0064 (3)	0.0069 (4)	0.0034 (1)	−0.0037 (6)	0.0019 (3)	−0.0008 (4)
C1	0.7083 (5)	0.0890 (5)	0.3003 (3)	0.0055 (4)	0.0064 (5)	0.0028 (2)	0.0016 (8)	0.0002 (5)	−0.0005 (5)
C2	0.6139 (5)	−0.0617 (6)	0.2189 (3)	0.0054 (4)	0.0078 (6)	0.0026 (2)	0.0017 (9)	0.0003 (5)	−0.0004 (5)
C3	0.5391 (6)	−0.0406 (6)	0.3199 (3)	0.0088 (5)	0.0054 (5)	0.0027 (2)	−0.0001 (9)	0.0013 (5)	−0.0011 (5)
C4	0.3262 (5)	0.1985 (6)	0.3120 (3)	0.0059 (4)	0.0074 (5)	0.0028 (2)	−0.0024 (9)	0.0004 (5)	−0.0003 (5)
C5	0.3463 (5)	0.2610 (6)	0.1954 (3)	0.0048 (4)	0.0078 (6)	0.0027 (2)	0.0007 (6)	0.0007 (4)	−0.0001 (5)
C6	0.3419 (5)	0.0325 (6)	0.2418 (3)	0.0050 (4)	0.0078 (6)	0.0029 (2)	−0.0031 (8)	0.0009 (5)	−0.0007 (5)
C7	0.5042 (4)	0.1328 (5)	0.1863 (5)	0.0045 (3)	0.0045 (4)	0.0021 (1)	−0.0001 (7)	0.0002 (4)	0.0002 (4)
C8	0.5984 (4)	0.1923 (5)	0.1938 (3)	0.0041 (3)	0.0055 (4)	0.0021 (1)	0.0004 (7)	0.0008 (4)	0.0008 (4)
C9	0.5989 (4)	0.2997 (5)	0.2320 (3)	0.0039 (3)	0.0056 (4)	0.0022 (1)	−0.0000 (7)	0.0001 (4)	0.0004 (4)
C10	0.5199 (5)	0.3017 (5)	0.2786 (3)	0.0044 (4)	0.0047 (4)	0.0022 (1)	−0.0008 (7)	−0.0005 (4)	−0.0009 (4)
C11	0.5312 (5)	0.2002 (5)	0.3146 (3)	0.0042 (3)	0.0057 (4)	0.0021 (1)	−0.0013 (7)	0.0007 (4)	−0.0011 (4)
C12	0.5476 (5)	0.2013 (5)	0.3827 (3)	0.0062 (4)	0.0055 (4)	0.0020 (1)	−0.0001 (8)	0.0009 (4)	−0.0007 (4)
C13	0.6264 (6)	0.2698 (6)	0.4097 (3)	0.0065 (5)	0.0098 (6)	0.0027 (2)	0.0001 (10)	0.0002 (5)	−0.0025 (6)
C14	0.6454 (7)	0.2759 (8)	0.4733 (3)	0.0084 (6)	0.0138 (8)	0.0026 (2)	−0.0001 (13)	−0.0003 (6)	−0.0023 (7)
C15	0.5873 (7)	0.2147 (8)	0.5100 (3)	0.0118 (7)	0.0146 (9)	0.0024 (2)	0.0006 (15)	0.0003 (6)	−0.0041 (7)
C16	0.5100 (7)	0.1445 (7)	0.4863 (3)	0.0138 (8)	0.0095 (7)	0.0025 (2)	0.0059 (12)	0.0043 (6)	−0.0008 (6)
C17	0.4866 (6)	0.1361 (6)	0.4198 (3)	0.0087 (5)	0.0082 (6)	0.0023 (2)	0.0041 (9)	0.0023 (5)	0.0003 (5)
C18	0.6794 (5)	0.1864 (5)	0.1491 (3)	0.0045 (4)	0.0071 (5)	0.0020 (1)	−0.0012 (8)	0.0004 (4)	0.0006 (4)
C19	0.7557 (5)	0.1056 (6)	0.1516 (3)	0.0045 (4)	0.0085 (6)	0.0024 (2)	0.0007 (8)	0.0006 (4)	−0.0002 (5)
C20	0.8296 (5)	0.1074 (7)	0.1093 (3)	0.0051 (4)	0.0103 (7)	0.0029 (2)	−0.0018 (9)	0.0013 (5)	0.0003 (6)
C21	0.8252 (6)	0.1893 (7)	0.0627 (4)	0.0055 (4)	0.0135 (8)	0.0036 (2)	−0.0030 (11)	0.0029 (5)	0.0002 (7)
C22	0.7517 (6)	0.2748 (8)	0.0609 (4)	0.0068 (5)	0.0134 (8)	0.0031 (2)	−0.0023 (11)	0.0024 (5)	0.0027 (7)
C23	0.6782 (5)	0.2756 (7)	0.1041 (3)	0.0059 (4)	0.0109 (7)	0.0030 (2)	−0.0024 (10)	0.0016 (5)	0.0030 (6)
C24	0.4789 (5)	0.4174 (5)	0.2972 (3)	0.0047 (4)	0.0060 (5)	0.0029 (2)	−0.0012 (8)	−0.0002 (5)	−0.0011 (5)
C25	0.4334 (6)	0.4350 (6)	0.3507 (3)	0.0055 (4)	0.0085 (6)	0.0034 (2)	0.0006 (9)	0.0013 (5)	−0.0043 (5)
C26	0.3943 (6)	0.5431 (6)	0.3656 (4)	0.0060 (5)	0.0080 (6)	0.0048 (3)	0.0012 (10)	0.0001 (6)	−0.0037 (6)
C27	0.4000 (6)	0.6338 (6)	0.3244 (4)	0.0061 (5)	0.0082 (6)	0.0052 (3)	0.0027 (10)	−0.0019 (6)	−0.0043 (7)
C28	0.4430 (6)	0.6196 (6)	0.2707 (4)	0.0077 (5)	0.0077 (6)	0.0042 (2)	0.0004 (10)	−0.0022 (6)	−0.0019 (7)
C29	0.4829 (6)	0.5128 (6)	0.2559 (4)	0.0064 (5)	0.0053 (5)	0.0040 (2)	0.0006 (9)	−0.0016 (6)	0.0006 (6)
C30	0.4637 (5)	0.0785 (5)	0.1271 (3)	0.0047 (4)	0.0067 (5)	0.0020 (1)	0.0005 (8)	0.0007 (4)	−0.0005 (4)
C31	0.4265 (5)	−0.0353 (6)	0.1218 (3)	0.0054 (4)	0.0095 (6)	0.0028 (2)	−0.0010 (9)	0.0005 (5)	−0.0036 (5)
C32	0.3785 (6)	−0.0765 (7)	0.0651 (4)	0.0065 (5)	0.0130 (8)	0.0030 (2)	−0.0008 (11)	0.0002 (5)	−0.0044 (6)
C33	0.3685 (6)	−0.0046 (8)	0.0151 (4)	0.0070 (5)	0.0136 (8)	0.0027 (2)	0.0002 (12)	−0.0003 (5)	−0.0024 (7)
C34	0.4048 (6)	0.1085 (7)	0.0201 (3)	0.0057 (5)	0.0142 (8)	0.0028 (2)	0.0029 (11)	−0.0002 (5)	−0.0025 (7)
C35	0.4510 (5)	0.1502 (6)	0.0755 (3)	0.0051 (4)	0.0096 (6)	0.0021 (2)	0.0023 (9)	0.0000 (4)	0.0003 (5)
C36	−0.079 (2)	0.057 (2)	0.4824 (9)	7.6 (5)					
C37	−0.029 (2)	0.058 (2)	0.4647 (12)	10.3 (7)					
C38	0.102 (2)	−0.030 (2)	0.4830 (12)	10.7 (6)					
C39	0.025 (3)	0.001 (4)	0.4791 (13)	13.0 (10)					
C40	0.086 (2)	0.036 (2)	0.4359 (12)	10.2 (7)					
C41	0.011 (2)	0.086 (2)	0.4313 (12)	10.8 (7)					

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

or polyenyl group, to mention only the more familiar possibilities, and (4) the presence or absence of one or more bridging CO groups.

The general problem concerning this class of substances to which the results described below make one contribution is this: What kinds of carbonyl scrambling processes occur in such molecules and what rules can we discover to indicate (a) which ones are favored under various circumstances and (b) what their relative rates will be?

In fact, the problem defined as above is really even broader since it necessarily merges into the corresponding problems of carbonyl scrambling in mononuclear systems of the types **2** and **3** as well as into the behavior of polynuclear (M_3 and higher) systems.



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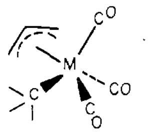
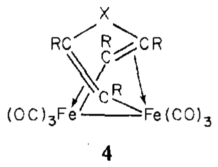


3

The particular molecule which we describe in detail here is of a type first described many years ago by W. Hübel and his coworkers at the Union Carbide European Research Associates, in Brussels.[1] The general structure is indicated by **4**. The group X is most often CO but it may also be an



4

ethylidine group, C=CH_2. The structures of two such substances have previously been determined by x-ray crystallography. One is the compound[2] with R = H and X = C=CH_2 (**4a**) while the other[3] has R = CH_3 and X = C=O (**4b**). The structures in the two cases are very similar although the two Fe–Fe distances differ somewhat more than might have been expected. They are 2.527 (6) Å for **4a** and 2.507 (8) Å for **4b**. There have not been any NMR data reported for any substance in this class.

In this paper we describe a study in which the compound with R = Ph and X = CO (**4c**) has been characterized by x-ray crystallography and the scrambling of its CO groups studied by ^{13}C NMR spectroscopy.

Experimental Section

Preparation. The title compound, **4c**, was prepared in greater than 80% yield (based on diphenylacetylene) by combining 5.0 g (0.013 mol) of diiron nonacarbonyl dried in vacuo with 2.3 g (0.013 mol) of diphenylacetylene in 100 ml of dry tetrahydrofuran. The reaction mixture was stirred for 4 hr under nitrogen at 23° to give a red-brown solution which was chromatographed on 100–200 mesh Florisil. A red-brown band was collected and taken to dryness in vacuo. Large crystals of $Fe_2(CO)_6C_4CO(C_6H_5)_4$ were grown by slowly cooling a hot saturated benzene solution of the above product. The infrared spectrum measured in methylcyclohexane has CO stretching bands at 2065, 2043, 2010, and 1662 cm^{-1}.

Collection of X-Ray Data. A crystal of $Fe_2(CO)_6C_4CO(C_6H_5)_4$ measuring 0.3 × 0.4 × 0.6 mm was mounted on a thin glass fiber. Preliminary examination of the crystal and data collection were performed on a Syntex $P\bar{1}$ computer-controlled diffractometer equipped with a graphite-crystal incident-beam monochromator. For the location of a set of starting reflections the diffractometer setting angles were positioned at $2\theta = \omega = \chi = 0°$ and a Polaroid film cassette was mounted in front of the counter at 9.8 cm from the crystal. The film was exposed to Mo Kα radiation for 15 min while the ϕ axis was rotated through 360° at 192°/min. From this film the x and y coordinates of 15 reflections were measured. These results were put into the computer, and, using the Syntex software package, the reflections were centered automatically. The setting angles for the reflections were used as input for the autoindexing program which is used to select the best unit cell. The crystal was found to be monoclinic and the space group was inferred to be $P2_1/n$. Cell constants (at 23°C) obtained from a least-squares refinement of the setting angles for 15 strong reflections are $a = 13.167$ (5) Å, $b = 11.535$ (3) Å, $c = 21.787$ (8) Å, $\beta = 95.11$ (2)°, and $V = 3295.9$ (9) Å^3. The width at half-height for ω scans of several strong reflections was 0.2°.

Intensity data were collected at 23° with Mo Kα radiation using the θ–2θ scan technique and a variable-scan rate of 4.0–24.0°/min depending on the intensity of the reflection. A symmetrical scan range of 2θ(Mo Kα_1) − 1.0° to 2θ(Mo Kα_2) + 1.0° was used to measure 6633 unique reflections up to a maximum 2θ of 50.0°. Stationary-crystal, stationary-counter background counts were taken at each end of the 2θ scan range; the total background counting time was equal to half the scan time. The Syntex data collection program corrects the scan count for background. For intense reflections a coincidence correction is automatically applied to the data. The counter was placed 18 cm from the crystal with counter aperture wide open at its 2-mm diameter. The linear absorption coefficient is 9.66 cm^{-1} and the transmission factors for all reflections varied from 67.9 to 74.5%. No absorption corrections were applied.

An x-ray beam collimator with a 1.5-mm opening was used. The takeoff angle going into the monochromator was set at 3° and the width of the pulse height analyzer set to accept about 95% of the radiation when centered on the Mo Kα peak. Three standard reflections were measured after every 100 reflections to check on crystal and electronic stability. No trends in the standards were observed. In the refinement of the structure 4277 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used. Here $\sigma(F_o^2)$ is the standard deviation for the observed intensity of a reflection and is calculated from the formula $\sigma(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]^{1/2}$ where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, and B is the total background count. The parameter p used in the calculation of standard deviations was set equal to 0.07.

Refinement of the Structure. The Enraf-Nonius structure determination package (SDP) with a PDP 11/45 computer was used to solve and refine the structure. The structure was solved by Patterson heavy-metal methods for the two iron atoms. A subsequent least-squares cycle and difference Fourier map produced the remaining 48 nonhydrogen atoms. The crystal was found to contain benzene of crystallization and thus the formula unit in the crystal is $[(C_6H_5)_4C_4CO]Fe_2(CO)_6\cdot{}^1/_2C_6H_6$. The benzene ring was found to be disordered around the inversion center and was therefore refined as six half carbon atoms.

Table II. Bond Distances (Å)[a]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Fe1	Fe2	2.536 (1)	C7	C30	1.490 (6)	C25	C26	1.398 (7)
Fe1	C1	1.812 (6)	C8	C9	1.493 (6)	C26	C27	1.386 (9)
Fe1	C2	1.834 (5)	C8	C18	1.509 (6)	C27	C28	1.353 (9)
Fe1	C3	1.809 (6)	C9	C10	1.516 (6)	C28	C29	1.389 (7)
Fe1	C7	2.071 (4)	C10	C11	1.410 (6)	C30	C31	1.403 (7)
Fe1	C8	2.179 (4)	C10	C24	1.510 (6)	C30	C35	1.394 (6)
Fe1	C11	2.050 (4)	C11	C12	1.481 (6)	C31	C32	1.418 (7)
Fe2	C4	1.818 (5)	C12	C13	1.391 (7)	C32	C33	1.366 (9)
Fe2	C5	1.795 (6)	C12	C17	1.407 (7)	C33	C34	1.390 (8)
Fe2	C6	1.803 (5)	C13	C14	1.389 (7)	C34	C35	1.388 (7)
Fe2	C7	2.018 (4)	C14	C15	1.353 (9)	C36	C37	0.79 (3)
Fe2	C10	2.159 (4)	C15	C16	1.365 (9)	C36	C39	1.52 (5)
Fe2	C11	2.033 (4)	C16	C17	1.458 (7)	C36	C41	1.73 (3)
O1	C1	1.115 (6)	C18	C19	1.368 (6)	C37	C39	1.00 (4)
O2	C2	1.121 (6)	C18	C23	1.420 (6)	C37	C40	1.71 (4)
O3	C3	1.119 (6)	C19	C20	1.397 (7)	C37	C41	0.99 (3)
O4	C4	1.152 (6)	C20	C21	1.385 (8)	C38	C39	1.08 (4)
O5	C5	1.136 (6)	C21	C22	1.380 (8)	C38	C40	1.28 (3)
O6	C6	1.128 (6)	C22	C23	1.409 (7)	C39	C40	1.35 (3)
O7	C9	1.213 (5)	C24	C25	1.372 (7)	C39	C41	1.43 (5)
C7	C8	1.414 (6)	C24	C29	1.425 (7)	C40	C41	1.14 (3)

[a] Numbers in parenthese are estimated standard deviations in the least significant digits.

The structure was refined anisotropically with the benzene ring isotropic to convergence by five full-matrix least-squares cycles to give the following discrepancy indices: $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o| = 0.064$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.097$. The terms $|F_o|$ and $|F_c|$ are observed and calculated structure factor amplitudes and w is the weighting factor, $4F_o^2/\sigma^2$, where σ is the esd of F_o^2. No unusual trends were found in the data as a function of $\lambda^{-1} \sin \theta$, $|F_o|$, Miller indices, or reflection number. Atomic scattering factors were taken from Vol. IV of the "International Tables for X-Ray Crystallography". A final difference Fourier map was found to be featureless indicating that all of the structure has been determined. A table of the observed and calculated structure factors is available as supplementary material.

NMR Measurements. These were made using a Jeol PFT 100/Nicolet 1080 Fourier transform spectrometer operating at a frequency of 25.035 MHz. A sweep width of 6000 Hz, at a tilt angle of 49°, repeated at 1.2-sec intervals was employed. The solvent employed was *sym*-tetrachloroethane containing $C_2Cl_4D_2$ for deuterium locking and CS_2 as a reference. Approximately 0.5 mg of tris(acetylacetonato)chromium was added to shorten the longitudinal relaxation time. Temperature calibration was accomplished by measuring temperatures in a sample tube filled with solvent with a copper–constantan thermocouple connected to a Leeds and Northup Model 913 digital thermometer. At any dial setting of the variable-temperature unit temperature was constant to ±2° over the time required to record a spectrum.

The compound was enriched in ^{13}CO by stirring a solution, in contact with the appropriate quantity of gaseous ^{13}CO, under uv illumination. The level of enrichment was monitored by examination of the ir spectrum in the CO stretching region. For the spectra used in line shape analysis enrichments of 15–20% were used.

Spectra were computer simulated for various residence times using a computer program DNMR3 written by D. A. Kleier and G. Binsch.[4]

Results

Structure. The molecular structure is the anticipated one of type **4**. The positional and thermal parameters of the atoms are listed in Table I. The atoms listed as C36–C41, and refined only isotropically, are half-atoms constituting the disordered molecule of benzene of solvation.

The molecular structure is displayed in Figures 1 and 2. A monoptic view in which the phenyl rings are omitted (Figure 1) shows the conformation of the five-carbon chain which, in addition to the metal–metal bond, connects the iron atoms. The complete structure is displayed in the stereopair. The bond distances are listed in Table II and the bond angles in Table III. Although the structure possesses no rigorous (crystal-

Table III. Bond Angles (deg)[a]

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Fe2	Fe1	C1	138.4 (2)	Fe2	C6	O6	175.5 (5)	C24	C25	C26	121.8 (6)
Fe2	Fe1	C2	124.4 (2)	Fe1	C7	Fe2	76.7 (2)	C25	C26	C27	118.7 (6)
Fe2	Fe1	C3	94.1 (2)	Fe1	C7	C8	74.7 (3)	C26	C27	C28	121.3 (5)
Fe2	Fe1	C7	50.7 (1)	Fe1	C7	C30	131.7 (3)	C27	C28	C29	120.3 (6)
Fe2	Fe1	C8	75.4 (1)	Fe2	C7	C8	114.1 (3)	C24	C29	C28	120.1 (6)
Fe2	Fe1	C11	51.3 (1)	Fe2	C7	C30	120.3 (3)	C7	C30	C31	124.1 (4)
C1	Fe1	C2	95.8 (2)	C8	C7	C30	123.2 (4)	C7	C30	C35	117.2 (4)
C1	Fe1	C3	98.7 (2)	Fe1	C8	C7	66.5 (2)	C31	C30	C35	118.2 (5)
C1	Fe1	C7	130.6 (2)	Fe1	C8	C9	99.5 (3)	C30	C31	C32	120.7 (5)
C1	Fe1	C8	92.0 (2)	Fe1	C8	C18	123.9 (3)	C31	C32	C33	119.7 (6)
C1	Fe1	C11	88.7 (2)	C7	C8	C9	115.3 (4)	C32	C33	C34	119.8 (5)
C2	Fe1	C3	86.7 (2)	C7	C8	C18	124.5 (4)	C33	C34	C35	121.0 (6)
C2	Fe1	C7	88.4 (2)	C9	C8	C18	115.5 (4)	C30	C35	C34	120.5 (5)
C2	Fe1	C8	95.7 (2)	O7	C9	C8	123.5 (4)	C37	C36	C39	36.2 (27)
C2	Fe1	C11	175.5 (2)	O7	C9	C10	121.7 (4)	C37	C36	C41	15.6 (30)
C3	Fe1	C7	130.7 (2)	C8	C9	C10	114.6 (4)	C39	C36	C41	51.7 (19)
C3	Fe1	C8	168.8 (2)	Fe2	C10	C9	107.1 (3)	C36	C37	C39	115.7 (46)
C3	Fe1	C11	92.0 (2)	Fe2	C10	C11	65.6 (2)	C36	C37	C40	168.1 (42)
C7	Fe1	C8	38.8 (2)	Fe2	C10	C24	117.3 (3)	C36	C37	C41	152.0 (54)
C7	Fe1	C11	89.1 (2)	C9	C10	C11	108.4 (4)	C39	C37	C40	52.4 (26)
C8	Fe1	C11	84.7 (2)	C9	C10	C24	118.4 (4)	C39	C37	C41	92.1 (41)
Fe1	Fe2	C4	127.1 (2)	C11	C10	C24	127.4 (4)	C40	C37	C41	39.7 (22)
Fe1	Fe2	C5	135.8 (2)	Fe1	C11	Fe2	76.8 (2)	C39	C38	C40	69.5 (24)
Fe1	Fe2	C6	91.8 (2)	Fe1	C11	C10	111.7 (3)	C36	C39	C37	28.1 (23)
Fe1	Fe2	C7	52.6 (1)	Fe1	C11	C12	120.6 (3)	C36	C39	C38	170.9 (31)
Fe1	Fe2	C10	75.4 (1)	Fe1	C11	C10	75.2 (3)	C36	C39	C40	120.0 (39)
Fe1	Fe2	C11	51.9 (1)	Fe2	C11	C12	135.0 (3)	C36	C39	C41	71.9 (31)
C4	Fe2	C5	95.6 (2)	C10	C11	C12	123.3 (4)	C37	C39	C38	152.3 (40)
C4	Fe2	C6	86.1 (2)	C11	C12	C13	117.7 (4)	C37	C39	C40	91.9 (40)
C4	Fe2	C7	179.7 (2)	C11	C12	C17	122.0 (4)	C37	C39	C41	43.9 (29)
C4	Fe2	C10	96.0 (2)	C13	C12	C17	120.2 (5)	C38	C39	C40	62.4 (26)
C4	Fe2	C11	88.6 (2)	C12	C13	C14	120.8 (5)	C38	C39	C41	109.8 (33)
C5	Fe2	C6	103.5 (2)	C13	C14	C15	120.2 (6)	C40	C39	C41	48.0 (16)
C5	Fe2	C7	84.7 (2)	C14	C15	C16	121.8 (6)	C37	C40	C38	83.4 (19)
C5	Fe2	C10	90.8 (2)	C15	C16	C17	120.0 (6)	C37	C40	C39	35.7 (20)
C5	Fe2	C11	129.8 (2)	C12	C17	C16	117.0 (5)	C37	C40	C41	34.0 (15)
C6	Fe2	C7	94.0 (2)	C8	C18	C19	124.3 (4)	C38	C40	C39	48.1 (21)
C6	Fe2	C10	165.2 (2)	C8	C18	C23	116.6 (4)	C38	C40	C41	117.2 (24)
C6	Fe2	C11	126.7 (2)	C19	C18	C23	119.0 (5)	C39	C40	C41	69.7 (28)
C7	Fe2	C10	83.9 (2)	C18	C19	C20	121.0 (5)	C36	C40	C37	12.4 (25)
C7	Fe2	C11	91.1 (2)	C19	C20	C21	120.5 (5)	C36	C41	C39	56.3 (21)
C10	Fe2	C11	39.2 (2)	C20	C21	C22	119.5 (5)	C36	C41	C40	118.6 (22)
Fe1	C1	O1	176.2 (5)	C21	C22	C23	120.5 (5)	C37	C41	C39	44.0 (20)
Fe1	C2	O2	176.1 (5)	C18	C23	C22	119.3 (5)	C37	C41	C40	106.3 (33)
Fe1	C3	O3	178.7 (5)	C10	C24	C25	123.6 (4)	C39	C41	C40	62.3 (22)
Fe2	C4	O4	173.9 (5)	C10	C24	C29	118.6 (5)				
Fe2	C5	O5	175.8 (5)	C25	C24	C29	117.8 (5)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

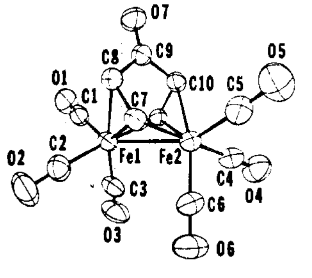


Figure 1. Central portion of the structure of the title compound. The phenyl groups have been omitted. Atoms are represented by their thermal vibration ellipsoids, drawn to enclose 50% of the electron density. C. K. Johnson's program ORTEP was used.

lographic) element of symmetry, it comes very close to having a twofold axis, passing through the keto group and bisecting the Fe–Fe bond.

Nuclear Resonance Results. Figure 3 shows the ^{13}C spectra in the carbonyl group region at several temperatures from −23 to +85°C. The enrichment level in this set of spectra is in the range 15–20% so that no molecules in which ^{13}C–^{13}C coupling might be expected are present at an observable concentration.

Also shown in Figure 3 are computer-simulated spectra computed on the assumption that the ^{13}C nucleus has the same residence time in each of the three CO environments. Calculated spectra have been matched, as shown, to observed spectra at several temperatures, and the rate vs. temperature data so obtained have been used to estimate the kinetic activation parameters. From an Arrhenius plot we obtained E_a = 14.7 (2) kcal mol^{-1} and A = 3.4 (8) × 10^{12} sec^{-1}. The appropriate quantities in the absolute reaction rate theory are $\Delta G^{\ddagger}$ = 15.1 (2) kcal mol^{-1} at 300 K, $\Delta H^{\ddagger}$ = 14.1 (1) kcal mol^{-1}, and $\Delta S^{\ddagger}$ = −3.2 (5) cal mol^{-1} deg^{-1}.

Discussion

If we assume that the molecule intrinsically has a diad symmetry axis, there are three types of carbonyl ligand present. One is approximately trans to the Fe–Fe bond, one approximately trans to the C–Fe bond, and one approximately trans to the olefin–iron bond. The three resonances for these types (each of the same width and intensity) are observed at and below −23°C. Above this temperature the resonances begin to broaden and at about +30°, as shown in Figure 3, coalescence to one broad line occurs. The observed pattern of broadening and collapse can be faithfully reproduced via computer simulation using a permutation matrix in which the

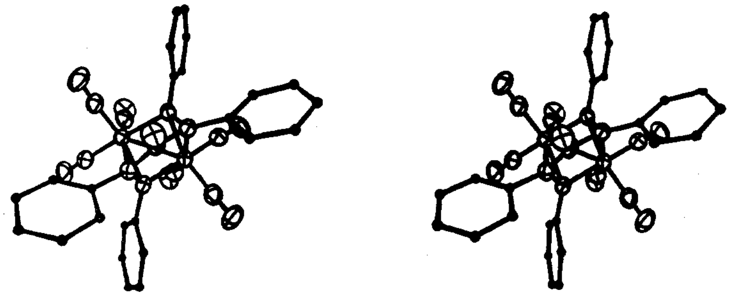


Figure 2. Stereoscopic view of the entire molecule of the title compound, drawn via C. K. Johnson's program ORTEP.

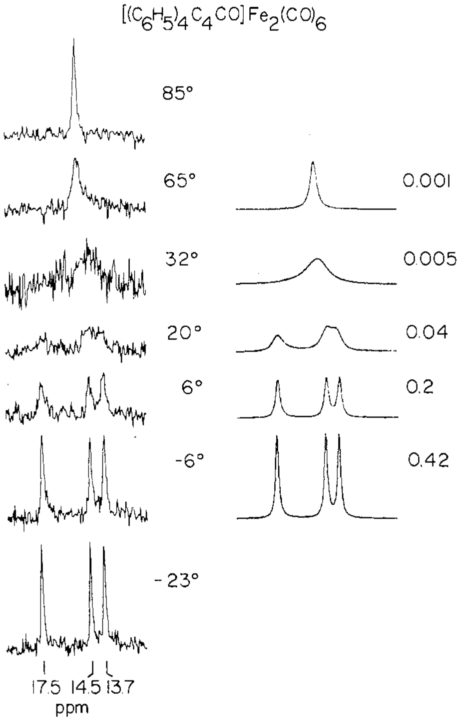


Figure 3. Carbon-13 NMR spectra for the title compound. Experimental spectra at various temperatures are shown on the left. The chemical shifts are in ppm downfield from internal CS_2. Computer-simulated spectra at various residence times (in sec) are shown at the right, matched to the experimental spectra at various temperatures.

^{13}C nucleus is assigned the same lifetime in each of the three types of site. Thus a scrambling process in which any two sites interchange more readily with each other than with the third is ruled out.

The results at hand are not sufficient to specify uniquely the scrambling process. There are two broad possibilities: (1) local scrambling of each set of three CO groups among themselves; (2) passage of CO groups from one metal atom to the other, via transient formation of bridges, in such a way as to allow all six CO groups to pass among all six positions. Previous work in this laboratory has shown that local scrambling, probably by a more or less rigid rotation of an $M(CO)_3$ group, is a common process[5-7] and thus it might well be operative here. However, in the absence of any direct evidence against internuclear scrambling in this case, the choice of mechanism, even between the two broad categories mentioned, cannot be made.

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Registry No. $[(C_6H_5)_4C_4CO]Fe_2(CO)_6$, 57214-94-5; diiron nonacarbonyl, 15321-51-4; diphenylacetylene, 501-65-5; ^{13}C, 14762-74-4.

Supplementary Material Available: Table of observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

References and Notes

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