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Metal–Metal Multiple Bonds in Organometallic Compounds. I. (Di-*tert*-butylacetylene)hexacarbonyldiiron and -dicobalt

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Abstract: The compound $[(CH_3)_3CC{\equiv}CC(CH_3)_3]Fe_2(CO)_6$ has been prepared and characterized structurally. It consists of two $Fe(CO)_3$ groups joined by a short, 2.316 (1) Å, iron–iron bond which can be formulated as a double bond. The compound forms black crystals belonging to the monoclinic system, space group $P2_1/n$, with unit cell dimensions $a = 13.824$ (4) Å, $b = 9.776$ (3) Å, $c = 13.826$ (5) Å, $\beta = 94.26$ (3)°, $V = 1863$ (1) Å^3, and $Z = 4$. The structure was solved and refined to final discrepancy indices of $R_1 = 0.049$ and $R_2 = 0.069$ using 1767 reflections having $I > 3\sigma(I)$ out of a total of 2442 reflections measured. For comparison, the corresponding cobalt compound, $(t\text{-BuC}_2)Co_2(CO)_6$, was also prepared and its structure determined. This should contain a Co–Co single bond and the Co–Co distance found is 2.463 (1) Å. The cobalt compound forms deep maroon crystals belonging to the triclinic system, space group $P\bar{1}$, with unit cell dimensions $a = 8.394$ (4) Å, $b = 8.491$ (6) Å, $c = 13.825$ (6) Å, $\alpha = 88.39$ (5)°, $\beta = 94.73$ (5)°, $\gamma = 106.86$ (4)°, $V = 940$ (1) Å^3, and $Z = 2$. The structure was refined to final discrepancy indices of $R_1 = 0.038$ and $R_2 = 0.062$, using 2246 reflections with $I > 3\sigma(I)$ out of a total of 2660 reflections measured. The two structures are very similar in most ways (e.g., the C≡C distances are 1.311 (10) and 1.335 (6) Å for the Fe and Co compounds, respectively) but differ in the relative orientations of the CO groups. In the cobalt compound the $Co_2(CO)_6$ group has virtual C_{2v} symmetry whereas in the iron compound one $Fe(CO)_3$ group is rotated by about 60° so that the $Fe_2(CO)_6$ group has only a mirror plane passing through the two iron atoms and two CO groups.

During the last 20 years a variety of compounds have been isolated from the reaction of acetylenes (R_2C_2) and various iron carbonyls.[1] These reactions tend to be complicated producing numerous products whose yields and compositions are dependent upon such things as temperature, reaction time, nature of the R group, etc. In addition, the majority of these complexes contain organic ligands which are no longer simple acetylenes but rather are cyclic derivatives of the acetylene employed. It is not surprising then to discover that only three types of simple acetylene-iron carbonyl complexes have been reported to date: $(R_2C_2)Fe(CO)_4$, R = $SiMe_3$,[1,2] *t*-Bu;[1,3] $(t\text{-Bu}_2C_2)_2Fe_2(CO)_4$;[4] and $(R_2C_2)Fe_2(CO)_6$[5] which appears to be identical in type with those previously formulated by Hubel and co-workers as $(R_2C_2)Fe_2(CO)_7$.[1]

We present here a full account of the synthesis and crystal structure of $(t\text{-Bu}_2C_2)Fe_2(CO)_6$, which was previously the subject of a short communication.[5] In addition, we report the results of a structure determination of the closely related $(t\text{-Bu}_2C_2)Co_2(CO)_6$. The latter study was undertaken because the structure of $(Ph_2C_2)Co_2(CO)_6$[6] had not been accurately determined. The structure of $(t\text{-Bu}_2C_2)Co_2(CO)_6$ was done, rather than a redetermination of the $(Ph_2C_2)Co_2(CO)_6$ structure, so that a very direct comparison with $(t\text{-Bu}_2C_2)Fe_2(CO)_6$ might be made.

Experimental Section

All operations were carried out in an atmosphere of dry nitrogen. Solvents were dried over potassium benzophenone and were distilled under nitrogen just prior to use. Diiron nonacarbonyl was purchased from Pressure Chemical Co., dicobalt octacarbonyl from Strem Chemical Co., and di-*tert*-butylacetylene, $t\text{-Bu}_2C_2$, 98%, from Chemical Samples Co. Infrared spectra were recorded on a Perkin-Elmer 237B spectrometer and were calibrated with polystyrene.

Synthesis of $(t\text{-Bu}_2C_2)Fe_2(CO)_6$. A mixture of 2.34 g (6.43 mmol) of $Fe_2(CO)_9$ and 0.89 g (6.4 mmol) of $t\text{-Bu}_2C_2$ in 40 ml of hexane was stirred at ambient temperature for 24 h. During this time the $Fe_2(CO)_9$ was consumed and the color of the solution became dark green. The reaction solution was filtered and the filtrate was then evaporated to dryness in vacuo at ambient temperature yielding 1.8 g (60%) of crude product. Black crystals of $(t\text{-Bu}_2C_2)Fe_2(CO)_6$ were obtained by recrystallization of the crude product from pentane at −40 °C. Yellow crystals of $(t\text{-Bu}_2C_2)Fe(CO)_4$ were also deposited[3] and were physically separated from the $(t\text{-Bu}_2C_2)Fe_2(CO)_6$ crystals. Ir (hexane): 2050, 2005, 1984, 1973 (sh), and 1968 (sh) cm^{-1}.

Synthesis of $(t\text{-Bu}_2C_2)Co_2(CO)_6$. This compound was prepared by allowing an equimolar mixture of $Co_2(CO)_8$ and $t\text{-Bu}_2C_2$ in hexane to react as previously described.[7,8] The crude product was recrystallized from pentane at −40 °C yielding large, deep maroon crystals. Ir (hexane): 2073, 2035, 2020, 2005, and 1990 cm^{-1}.

X-Ray Data Collection for $(t\text{-Bu}_2C_2)Fe_2(CO)_6$. A black crystal of $(t\text{-Bu}_2C_2)Fe_2(CO)_6$ measuring approximately 0.35 × 0.30 × 0.20 mm was sealed in a glass capillary. All data were collected at 21 ± 2 °C on a Syntex P$\bar{1}$ automated diffractometer using Mo Kα radiation monochromatized with a graphite crystal in the incident beam.

The automatic centering and autoindexing procedures followed have been described.[9] Systematic absences, of $h0l$ ($h + l \neq 2n$) and $0k0$ ($k \neq 2n$), indicated that the space group was $P2_1/n$. The principal crystallographic data are summarized as follows: $a = 13.824$ (4), $b = 9.776$ (3), $c = 13.826$ (5) Å; $\beta = 94.26$ (3)°; $V = 1863$ (1) Å^3; $d_{calcd} = 1.49$ g/cm^3 for $Z = 4$ and a molecular weight of 418.02.

A total of 2442 unique reflections with $0° < 2\theta \leq 45°$ were collected using the θ–2θ scan technique, variable scan rates from 4.0

Table I. Atomic Positional Parameters for $(t\text{-}Bu_2C_2)Fe_2(CO)_6$

	x	y	z
Fe1	0.5997 (1)	0.1874 (1)	0.2188 (1)
Fe2	0.4606 (1)	0.2504 (1)	0.1258 (1)
O1	0.7024 (5)	0.1450 (8)	0.4114 (5)
O2	0.7643 (5)	0.3129 (7)	0.1312 (5)
O3	0.6337 (5)	−0.0899 (7)	0.1470 (5)
O4	0.2814 (5)	0.1009 (8)	0.0698 (5)
O5	0.3763 (5)	0.4981 (7)	0.0333 (4)
O6	0.5706 (5)	0.1592 (7)	−0.0376 (4)
C1	0.6624 (6)	0.1612 (8)	0.3368 (6)
C2	0.6997 (6)	0.2637 (9)	0.1661 (6)
C3	0.6196 (5)	0.0172 (9)	0.1740 (5)
C4	0.3512 (6)	0.1606 (9)	0.0917 (6)
C5	0.4093 (5)	0.3989 (9)	0.0692 (5)
C6	0.5313 (6)	0.1927 (8)	0.0290 (6)
C7	0.5088 (5)	0.3417 (7)	0.2577 (5)
C8	0.4623 (5)	0.2278 (7)	0.2729 (5)
C9	0.5272 (5)	0.4872 (7)	0.2916 (5)
C10	0.5745 (7)	0.5727 (9)	0.2144 (6)
C11	0.4290 (7)	0.5508 (10)	0.3149 (8)
C12	0.5968 (6)	0.4825 (9)	0.3846 (5)
C13	0.3993 (6)	0.1541 (8)	0.3418 (5)
C14	0.4426 (7)	0.1726 (10)	0.4470 (6)
C15	0.2971 (7)	0.2195 (11)	0.3298 (8)
C16	0.3941 (8)	−0.0021 (9)	0.3177 (7)

to 24.0°/min, and a scan range from $2\theta(\text{Mo K}\alpha_1) - 0.9°$ to $2\theta(\text{Mo K}\alpha_2) + 0.9°$. Intensities of three standard reflections measured after every 100 reflections showed no significant variation during data collection. Lorentz and polarization corrections were applied,[10] but no absorption correction was deemed necessary since the linear absorption coefficient is 4.06 cm^{-1}.

Solution and Refinement of $(t\text{-}Bu_2C_2)Fe_2(CO)_6$. The position of each iron atom was determined using a three-dimensional Patterson function.[10] These coordinates were refined by two cycles of least-squares refinement to give discrepancy factors of

$$R_1 = (\sum||F_o| - |F_c||)/\sum|F_o| = 0.327$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.414$$

The function, $\Sigma w(|F_o| - |F_c|)^2$, was minimized with the weighting factor, w, equal to $4F_o^2/\sigma(F_o^2)^2$. All structure factor calculations and least-squares refinements were executed using only those 1767 reflections for which $F_o^2 > 3\sigma(F_o^2)$. Atomic scattering factors were those of Cromer and Waber.[11] Anomalous dispersion effects were included in the calculated scattering factors for iron.[12]

After refining both iron positions, a difference Fourier map revealed the positions of all remaining non-hydrogen atoms. The positions of all non-hydrogen atoms were refined isotropically by three full-matrix least-squares cycles giving discrepancy factors of $R_1 = 0.076$ and $R_2 = 0.109$. The entire structure was refined to convergence in four full-matrix least-squares cycles, refining all non-hydrogen atoms anisotropically. The final discrepancy factors were $R_1 = 0.049$ and $R_2 = 0.069$. The error in an observation of unit weight was 1.574. A final difference Fourier map showed no peaks above 0.38 e/Å^3. The peaks observed were in the regions expected for hydrogen atoms.

Data Collection for $(t\text{-}Bu_2C_2)Co_2(CO)_6$. The same general procedure used in the collection of data for $(t\text{-}Bu_2C_2)Fe_2(CO)_6$ was used for $(t\text{-}Bu_2C_2)Co_2(CO)_6$, and only deviations from the previous procedure are mentioned here.

A deep maroon crystal of $(t\text{-}Bu_2C_2)Co_2(CO)_6$ measuring approximately 0.32 × 0.29 × 0.25 mm was cut from a much larger crystal and then sealed in a glass capillary. Data were collected at 21 ± 2 °C. The unit cell was found to be triclinic with the following properties: space group $P\bar{1}$; $a = 8.394$ (4), $b = 8.491$ (6), $c = 13.825$ (6) Å; $\alpha = 88.39$ (5), $\beta = 94.73$ (5), $\gamma = 106.86$ (4)°; $V = 940$ (1) Å^3; $d_{calcd} = 1.50$ g/cm^3 for $Z = 2$ and mol wt = 424.19. A total of 2660 unique reflections were collected but only those 2246 reflections for which $F_o^2 > 3\sigma(F_o^2)$ were used in the subsequent refinement.

Solution and Refinement of $(t\text{-}Bu_2C_2)Co_2(CO)_6$. A three-dimensional Patterson function was calculated and the position of each cobalt atom was located. Two cycles of least-squares refinement gave $R_1 = 0.343$ and $R_2 = 0.440$. The positions of all other non-hydrogen atoms were found in a subsequent difference electron density map. After three cycles of isotropic least-squares refinement $R_1 = 0.073$ and $R_2 = 0.116$. The structure was then anisotropically refined to convergence in four cycles of full-matrix least-squares refinement with $R_1 = 0.038$ and $R_2 = 0.062$. Tables of observed and calculated structure factor amplitudes are available.[13]

Results

The Preparation of $(t\text{-}Bu_2C_2)Fe_2(CO)_6$. The reaction of $Fe_2(CO)_9$ with 2,2,5,5-tetramethylhex-3-yne, $t\text{-}Bu_2C_2$, gives $(t\text{-}Bu_2C_2)Fe_2(CO)_6$ as the main product, but an appreciable amount of the mononuclear product $(t\text{-}Bu_2C_2)Fe(CO)_4$ is also formed. The two compounds are sufficiently similar in their physical and solubility properties to make

Table II. Thermal Parameters for $(t\text{-}Bu_2C_2)Fe_2(CO)_6$[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{iso}[b]
Fe1	2.84 (4)	2.88 (5)	3.27 (4)	0.28 (3)	0.03 (3)	−0.14 (4)	2.98
Fe2	3.04 (4)	3.76 (5)	2.72 (4)	−0.07 (3)	0.17 (3)	−0.18 (4)	3.14
O1	7.2 (4)	8.8 (5)	4.3 (3)	2.1 (3)	−1.7 (3)	0.2 (3)	6.1
O2	4.4 (3)	6.8 (4)	9.3 (4)	−0.1 (3)	2.1 (3)	1.6 (2)	6.2
O3	7.3 (4)	3.7 (3)	7.1 (4)	0.5 (3)	0.0 (3)	−1.4 (3)	5.6
O4	5.6 (4)	9.1 (5)	6.7 (4)	−3.2 (3)	−0.7 (3)	−0.9 (3)	6.4
O5	6.9 (4)	5.4 (4)	6.0 (3)	1.2 (3)	−1.1 (3)	0.8 (3)	5.9
O6	6.4 (3)	7.5 (4)	3.9 (3)	0.7 (3)	1.6 (3)	−1.3 (3)	5.4
C1	4.7 (4)	4.1 (4)	4.4 (4)	1.1 (3)	0.2 (3)	0.2 (3)	4.3
C2	3.5 (4)	4.4 (4)	5.2 (4)	1.2 (3)	0.2 (3)	−0.1 (3)	4.2
C3	3.8 (4)	3.6 (4)	4.5 (4)	−0.1 (3)	−0.1 (3)	−0.4 (3)	3.9
C4	3.9 (4)	5.4 (5)	4.0 (4)	−0.6 (4)	0.2 (3)	0.2 (3)	4.4
C5	3.6 (4)	4.7 (5)	3.4 (3)	−0.5 (3)	−0.5 (3)	−0.5 (3)	3.8
C6	4.6 (4)	3.9 (4)	4.0 (4)	−0.7 (3)	−0.4 (3)	0.0 (3)	4.1
C7	3.3 (3)	3.3 (4)	2.7 (3)	0.3 (3)	0.3 (2)	−0.5 (2)	3.0
C8	3.5 (3)	3.1 (4)	3.0 (3)	−0.1 (3)	0.5 (2)	0.2 (2)	3.1
C9	3.3 (3)	2.3 (3)	4.1 (3)	−0.2 (3)	0.2 (3)	−0.7 (3)	3.1
C10	6.9 (5)	3.6 (4)	5.5 (5)	−1.8 (4)	1.2 (4)	0.6 (3)	4.8
C11	4.8 (4)	4.2 (5)	9.5 (6)	1.1 (4)	0.6 (4)	−2.1 (4)	5.4
C12	5.7 (5)	4.9 (5)	3.9 (4)	−0.9 (4)	−1.6 (3)	−1.2 (3)	4.4
C13	4.3 (4)	5.0 (5)	3.7 (4)	−0.9 (3)	0.9 (3)	0.7 (3)	4.1
C14	7.7 (6)	6.6 (6)	3.2 (6)	−1.6 (4)	1.5 (4)	0.4 (3)	5.2
C15	4.2 (4)	8.5 (7)	8.4 (6)	−0.7 (4)	2.4 (4)	0.9 (5)	6.3
C16	10.7 (7)	3.5 (4)	6.6 (5)	−3.1 (5)	2.4 (5)	0.2 (4)	5.5

[a] The B_{ij} in Å^2 is related to the dimensionless β_{ij} employed during refinement by $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [b] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Atomic Positional Parameters for $(t\text{-Bu}_2C_2)Co_2(CO)_6$

	x	y	z
Co1	0.2459 (1)	0.0510 (1)	0.2415 (1)
Co2	0.1002 (1)	0.2408 (1)	0.1642 (1)
O1	0.5036 (7)	0.0253 (7)	0.3722 (4)
O2	0.3210 (6)	−0.0880 (5)	0.0629 (3)
O3	−0.0411 (6)	−0.2104 (4)	0.3066 (3)
O4	−0.2432 (5)	0.0351 (5)	0.1886 (3)
O5	0.1453 (5)	0.1960 (5)	−0.0418 (3)
O6	0.0380 (6)	0.5606 (5)	0.1417 (4)
C1	0.4047 (7)	0.0065 (6)	0.3222 (4)
C2	0.2945 (7)	−0.0330 (6)	0.1319 (4)
C3	0.0682 (7)	−0.1091 (6)	0.2812 (4)
C4	−0.1098 (6)	0.1142 (6)	0.1788 (4)
C5	0.1285 (6)	0.2117 (6)	0.0373 (4)
C6	0.0643 (6)	0.4380 (6)	0.1520 (4)
C7	0.3299 (5)	0.2953 (5)	0.2299 (3)
C8	0.2184 (5)	0.2564 (5)	0.2964 (3)
C9	0.4943 (6)	0.4115 (6)	0.2050 (4)
C10	0.5549 (7)	0.3594 (7)	0.1119 (4)
C11	0.4761 (8)	0.5865 (7)	0.1893 (6)
C12	0.6251 (7)	0.4117 (8)	0.2909 (5)
C13	0.1780 (7)	0.2996 (6)	0.3957 (3)
C14	0.2900 (8)	0.2435 (9)	0.4748 (4)
C15	0.2121 (10)	0.4877 (8)	0.4015 (5)
C16	−0.0073 (7)	0.2119 (9)	0.4134 (4)

separation difficult. Although it may be possible to do so, we have not found an efficient chromatographic separation. Physical sorting of the yellow and black crystals is actually the most effective method of separation we have found for small scale use.

Structures of the $(t\text{-Bu}_2C_2)M_2(CO)_6$ Compounds. The atomic positional parameters are reported in Table I and the thermal parameters in Table II for the iron compound. The structure is depicted and the atom numbering scheme shown in Figure 1. The crystal consists of a normal packing of such molecules with no unusual intermolecular contacts.

For the cobalt compound the positional parameters and thermal parameters are listed in Tables III and IV, respectively, and the molecular structure is depicted in Figure 2. Again, the crystal packing involves no unusual contacts.

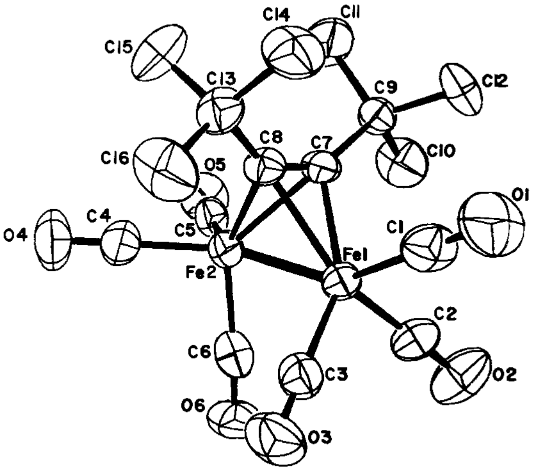


Figure 1. The molecular structure of $(t\text{-Bu}_2C_2)Fe_2(CO)_6$. Atoms are represented by their ellipsoids of thermal vibration scaled to enclose 50% of the electron density.

The atom numbering schemes of the two molecules have been made as similar as possible. The only differences are in the three carbonyl groups bound to Fe(2) and Co(2), since the orientations of these CO groups differ for the two molecules.

In order to facilitate comparisons, the interatomic distances for both molecules are listed in parallel columns in Table V. Also listed in this table are some of the dimensions for the similar molecule $(Ph_2C_2)Co_2(CO)_6$, the first molecule of this general type to have been structurally characterized by x-ray crystallography.[6] Bond angles for the same three molecules are listed in Table VI.

The structures of the iron and cobalt compounds differ very little aside from the difference in M–M bond lengths, and the difference in orientation of CO groups about M(2). There is, however, one other difference which should be noted. In the cobalt compound, the four bonds from metal atoms to acetylenic carbon atoms are equal within the experimental accuracy. Thus the four-atom, quasi-tetrahedral unit, C(7), C(8), Co(1), Co(2), has C_{2v} symmetry. In the iron compound this is not the case. There is a small twist of

Table IV. Thermal Parameters for $(t\text{-Bu}_2C_2)Co_2(CO)_6$[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{iso}[b]
Co1	3.33 (3)	2.39 (3)	3.25 (3)	0.98 (2)	0.31 (2)	0.17 (2)	2.91
Co2	2.79 (3)	2.75 (3)	3.06 (3)	0.91 (2)	−0.08 (2)	−0.06 (2)	2.84
O1	8.5 (3)	9.9 (3)	7.8 (3)	5.7 (3)	−2.0 (2)	1.3 (2)	7.1
O2	10.3 (3)	6.0 (2)	5.8 (2)	3.8 (2)	2.3 (2)	−1.0 (2)	6.2
O3	7.4 (3)	4.0 (2)	8.3 (3)	−0.6 (2)	2.8 (2)	0.3 (2)	6.1
O4	3.5 (2)	6.0 (2)	8.1 (3)	0.4 (2)	0.8 (2)	−0.8 (2)	5.6
O5	7.1 (2)	6.7 (2)	3.5 (2)	2.1 (2)	0.3 (2)	−0.5 (1)	5.4
O6	7.7 (3)	4.5 (2)	10.8 (3)	3.4 (2)	−0.5 (2)	0.3 (2)	6.4
C1	5.5 (3)	4.3 (3)	4.8 (3)	2.4 (2)	−0.4 (2)	0.2 (2)	4.6
C2	5.5 (3)	3.5 (2)	4.6 (3)	2.0 (2)	0.9 (2)	0.5 (2)	4.2
C3	5.1 (3)	3.0 (2)	4.6 (2)	0.9 (2)	0.9 (2)	0.3 (2)	4.1
C4	3.2 (2)	3.6 (2)	4.6 (2)	1.0 (2)	0.0 (2)	−0.7 (2)	3.7
C5	3.8 (2)	3.6 (2)	3.7 (2)	1.1 (2)	−0.2 (2)	0.1 (2)	3.7
C6	4.3 (3)	3.3 (2)	5.5 (3)	1.5 (2)	−0.3 (2)	−0.2 (2)	4.2
C7	2.9 (2)	2.5 (2)	3.2 (2)	0.9 (2)	−0.1 (2)	0.0 (1)	2.9
C8	3.0 (2)	2.5 (2)	3.0 (2)	0.8 (1)	−0.1 (2)	0.0 (1)	2.9
C9	3.1 (2)	3.1 (2)	5.8 (3)	0.4 (2)	0.3 (2)	0.1 (2)	3.9
C10	4.0 (3)	6.3 (3)	4.8 (3)	0.3 (2)	1.8 (2)	0.3 (2)	4.8
C11	5.7 (3)	3.1 (2)	11.3 (5)	−0.1 (2)	2.3 (3)	1.9 (3)	5.6
C12	3.2 (2)	8.0 (4)	6.2 (3)	−0.4 (2)	−1.1 (2)	−0.3 (3)	5.4
C13	5.1 (3)	4.2 (2)	3.3 (2)	1.6 (2)	−0.2 (2)	−0.8 (2)	4.0
C14	6.3 (3)	9.5 (4)	2.7 (2)	2.9 (3)	−0.4 (2)	−0.1 (2)	5.3
C15	11.0 (5)	4.8 (3)	5.9 (3)	2.6 (3)	1.5 (3)	−1.8 (2)	6.1
C16	4.5 (3)	8.7 (4)	4.3 (3)	1.5 (3)	2.0 (2)	−0.6 (2)	5.1

[a] The B_{ij} in Å^2 is related to the dimensionless β_{ij} employed during refinement by $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [b] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

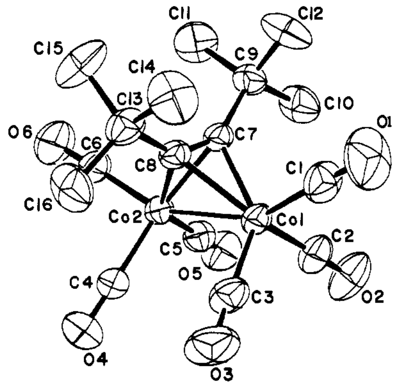


Figure 2. The molecular structure of (t-Bu_2C_2)$Co_2(CO)_6$. Thermal ellipsoids enclose 50% of the electron density.

Table V. Bond Lengths (Å) for $(R_2C_2)M_2(CO)_6$ Complexes

	M = Fe, R = t-Bu	M = Co, R = t-Bu	M = Co, R = Ph[a]
M1–M2	2.316 (1)	2.463 (1)	2.47
–C1	1.808 (9)	1.786 (5)	1.72
–C2	1.774 (10)	1.816 (4)	1.80
–C3	1.804 (9)	1.815 (5)	1.71
M2–C4	1.781 (9)	1.803 (5)	1.79
–C5	1.772 (9)	1.823 (5)	1.76
–C6	1.806 (9)	1.786 (5)	1.71
M1–C7	2.060 (7)	1.994 (4)	1.89
–C8	2.130 (7)	2.003 (4)	1.93
M2–C7	2.094 (7)	1.992 (4)	2.02
–C8	2.044 (7)	1.995 (4)	2.01
C7–C8	1.311 (10)	1.335 (6)	1.369[b]
–C9	1.513 (10)	1.505 (6)	1.43
C8–C13	1.519 (10)	1.520 (8)	1.42
C–O (av)	1.150	1.133	1.16

[a] Taken from ref 6. [b] Sly originally reported a C≡C bond length of 1.46 Å[6] but after further refinement a value of 1.369 Å was obtained.[14]

the C(7)-C(8) line relative to the Fe(1)-Fe(2) line so that the symmetry is lowered to C_2, and there are two long Fe-C distances (2.09, 2.13 Å) and two short ones (2.04, 2.06 Å). Perhaps the immediate cause of this twist is a distortion in the O(4)-C(4)-Fe(2)-C(5)-O(5) group such that C(5) makes a fairly close contact (3.38 Å) with C(10). This contact would be even closer were it not for the twist of the acetylene which is in the direction tending to mitigate the C(5)-C(10) contact. Since there would not appear to be any electronic reason for these distortions, we shall assume that they arise because of intramolecular nonbonded contacts. Thus, the only differences between the two structures which will be examined in the Discussion section will be the M-M bond lengths and the carbonyl configurations on M(2).

Discussion

Electronic Structure of the Iron Compound. The structure and composition of (t-Bu_2C_2)$Fe_2(CO)_6$ imply that there is a bond of order 2 between the iron atoms. This conclusion can be reached directly by considering how each iron atom can attain an 18-electron configuration. If the bridging acetylene is assumed to contribute two π electrons to each metal atom and the three CO groups are taken as donating a total of six electrons to the metal atom to which they are bound, then each metal atom will have a total of 16 electrons, counting its own eight, before the metal-metal interaction is taken into account. In order for each iron atom to reach an 18-electron count, each one will have to contribute two electrons to an iron-iron double bond.

Table VI. Bond Angles (deg) for $(R_2C_2)M_2(CO)_6$

	M = Fe	M = Co	M = Co, R = Ph[a]
M2–M1–C1	149.4 (3)	152.4 (2)	—
–C2	107.5 (3)	98.2 (2)	96
–C3	101.3 (2)	99.6 (2)	100
M1–M2–C4	132.0 (3)	97.2 (2)	97
–C5	138.7 (2)	99.7 (2)	100
–C6	81.7 (2)	151.9 (2)	—
C7–M1–C1	97.4 (3)	101.9 (2)	95
–C2	108.0 (3)	106.6 (2)	—
–C3	151.2 (3)	140.6 (2)	—
C8–M1–C1	95.1 (3)	103.5 (2)	103
–C2	144.0 (3)	142.5 (2)	—
–C3	117.0 (3)	103.4 (2)	—
C7–M2–C4	130.5 (3)	141.2 (2)	—
–C5	97.3 (3)	104.4 (2)	—
–C6	128.6 (3)	102.5 (2)	100
C8–M2–C4	99.1 (3)	105.3 (2)	—
–C5	120.2 (3)	141.7 (2)	—
–C6	137.5 (3)	101.6 (2)	104
C1–M1–C2	95.4 (4)	97.7 (2)	—
–C3	96.0 (3)	98.4 (2)	—
C2–M1–C3	95.9 (4)	103.6 (2)	—
C4–M2–C5	89.0 (4)	103.5 (2)	—
–C6	98.3 (4)	99.7 (2)	—
C5–M2–C6	98.6 (4)	97.6 (2)	—
M2–M1–C7	56.8 (2)	51.8 (1)	53
–C8	54.5 (2)	51.8 (1)	53
M1–M2–C7	55.4 (2)	51.9 (1)	49
–C8	58.1 (2)	52.1 (1)	50
M1–C7–M2	67.8 (2)	76.3 (1)	78
M1–C8–M2	67.4 (2)	76.1 (1)	77
C7–M1–C8	36.4 (3)	39.0 (2)	45
C7–M2–C8	36.9 (3)	39.1 (2)	43
M1–C7–C8	74.7 (4)	70.8 (3)	69
M1–C8–C7	68.9 (4)	70.2 (3)	66
M2–C7–C8	69.5 (4)	70.6 (3)	68
M2–C8–C7	73.6 (4)	70.3 (3)	69
C8–C7–C9	145.3 (6)	144.5 (4)	139
C7–C8–C13	144.6 (7)	144.8 (4)	137
M–C–O (av)	177.0	178.6	176

[a] Taken from ref 6.

Essentially the same sort of arithmetic has long been accepted in deducing the existence of single bonds between metal atoms in binuclear metal carbonyls and their derivatives. In fact, the compounds (t-Bu_2C_2)$Co_2(CO)_6$ and $(Ph_2C_2)Co_2(CO)_6$ are cases in point.

If the existence of a Co-Co single bond is accepted in (t-Bu_2C_2)$Co_2(CO)_6$ then a comparison of the metal-metal distances in the iron and cobalt compounds clearly argues for a double bond in the iron compound. Since the iron atom should be at least slightly larger than the cobalt atom, the Co-Co single bond distance of 2.46 Å implies that an Fe-Fe single bond distance within the same—or very similar—molecular environment should have a length of $\geq$2.50 Å. It is, of course, well known that nearly all Fe-Fe single bonds in a variety of compounds of the same general class have lengths[15] in the range 2.50-2.70 Å. Therefore, the observed Fe-Fe distance is about 0.20 Å shorter than one would expect for a single bond and this seems a reasonable shortening to associate with an increase in the bond order from 1 to 2.

The difference in the arrangement of the three CO groups on Fe(2) as compared to the arrangement on Co(2) seems likely to be of steric origin. The only basis for an electronic origin would be the orbital requirements of the double Fe═Fe bond as compared to the single Co—Co bond. If that were the causative factor it might be expected that the $Fe(CO)_3$ orientations would be changed on both ends of the molecule rather than only on one end. We propose instead the following steric explanation.

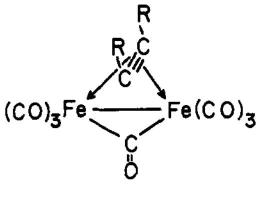
The arrangement of CO groups that occurs in the cobalt compound is such as to provide a distorted octahedral arrangement of six bonds about each metal atom, provided we choose to consider each metal to acetylene carbon atom interaction as a discrete bond. This symmetrical disposition of bonds is probably the most favorable one for each metal atom individually, but leads to one unfavorable feature in the context of the dinuclear molecule as a whole. It results in two pairs of CO groups being directly opposite each other, as can be seen in Figure 2. Evidently, whatever repulsive forces are engendered by this arrangement are tolerable in the cobalt compound. However, if this arrangement were to be maintained in the iron compound, where the metal atoms tend to approach each other much more closely, there would be considerably greater repulsive forces between the eclipsed CO groups on the two metal atoms. Evidently it is energetically preferable for the $Fe(CO)_3$ group on one end to rotate by about 60° so as to produce a staggering or interleaving of the CO groups.

This rotation is, of course, not without two penalties, but it can be argued that both of these penalties are likely to be small. The arrangement on Fe(2) tends to bring the two CO groups, C(4)-O(4) and C(5)-O(5), closer to the *tert*-butyl groups than is C(1)-O(1) on Fe(1). However, as already noted, there is considerable distortion in the molecule, apparently imposed by intramolecular contacts. Unambiguous evaluation of the probable importance of increased repulsion between carbonyl groups and atoms of the acetylene moiety as a result of the rotation of the $Fe(2)(CO)_3$ group is thus unavailable. We would not expect this increase to be large, however.

The other penalty arises from converting the arrangement of bonds about Fe(2) from a quasi-octahedral one to a quasi-prismatic one. It can be argued, however, that the unfavorable energy change associated with this is unlikely to be more than 12 kcal/mol and may well be less. The basis for this estimate is in the activation energies which have been measured for the process of rotation of $Fe(CO)_3$ groups against the remaining ligand atoms in a variety of compounds containing the $Fe(CO)_3$ or the $Fe_2(CO)_6$ groups coordinated by additional ligands of various types. For example, in compounds of the type $(OC)_3Fe(\mu\text{-}L)_2Fe(CO)_3$ where μ-L is PMe_2, $AsMe_2$, SEt, the activation energies for scrambling of the CO groups are about 10 kcal/mol.[17] In a variety of other compounds in which one $Fe(CO)_3$ or two of them united by an Fe-Fe bond are attached to some organic residue, the activation energies are in the range of, roughly, 8-12 kcal/mol.[18] Since the scrambling of the CO groups in all of these compounds is assumed to result from an essentially rigid rotation of the pyramidal $Fe(CO)_3$ unit against the rest of the molecule, the activation energy is a measure of how much less stable the molecule is when the rotation has proceeded approximately halfway to the next equivalent configuration, namely, by 60°. Thus, these activation energies correspond closely to the energy of rotation we are attempting to estimate in the comparison of the $(t\text{-}Bu_2C_2)Fe_2(CO)_6$ structure with the $(t\text{-}Bu_2C_2)Co_2(CO)_6$ structure.

It does not seem unreasonable to us that the increase in repulsion energy that would result from merely contracting the M-M bond length by 0.15 Å, as would be the case if the iron and cobalt compounds were strictly isostructural, could exceed 12 kcal/mol, thus making the rotation of one $M(CO)_3$ group energetically preferable.

Comparisons with Other Work. We can see no reason to doubt that the compound reported here as $(t\text{-}Bu_2C_2)Fe_2(CO)_6$ is the same one previously reported by Hubel[1] but assigned the formula $(t\text{-}Bu_2C_2)Fe_2(CO)_7$. The colors and infrared spectra of the two products appear to be the same within the accuracy of the description and the substance we have characterized as a hexacarbonyl is obtained when the preparative conditions indicated by Hubel are reproduced as closely as possible. Moreover, the formula assigned by Hubel (that is, with seven CO groups) is inconsistent with the infrared spectrum since the expected structure for the heptacarbonyl would be **1** and this would have a CO stretching band in the ir spectrum at a lower frequency than any observed. The structure suggested by Hubel, **2**, to account for the absence of a bridging CO band in the ir seems to us to be unsatisfactory since the presence of a donor Fe →Fe bond is arbitrary and unnecessary in view of the presumed availability of structure **1**. Even if structure **2** did occur, in a formal sense, one would expect that, as in numerous other cases in which there is a formally polar $^+M \rightarrow M^-$ bond, one or two CO groups would become "semibridging" CO groups and this would cause their stretching frequencies to drop to the range of 1900 cm^{-1} or less.[19,20]



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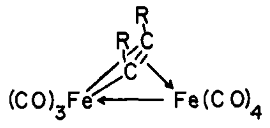

2

It would, therefore, appear that the first compounds containing the Fe-Fe double bond, namely, the $(R_2C_2)Fe_2(CO)_6$ species, were actually discovered in the early 1960's in Hubel's laboratory, but that their true nature went unrecognized. Thus, the first recognized example of an Fe=Fe double bond was reported only in 1971 when the compound $(t\text{-}Bu_2C_2)_2Fe_2(CO)_4$ was reported and its structure described.[4] The reported Fe=Fe distance is 2.215 Å, which is about 0.10 Å shorter than that in our compound. We suspect that this can be attributed to the replacement of two terminal CO groups by one bridging acetylene, which substantially lessens internal repulsions and may even have the effect of drawing the metal atoms together. Another compound of the same $(acetylene)_2Fe_2(CO)_4$ type was later reported[21] and this has an Fe=Fe distance of 2.225 Å. One more compound containing an Fe=Fe double bond[22] is $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}NO)_2$, where the metal-metal distance, 2.326 Å, is very similar to the present one.

In conclusion, we should like to observe that the bridging acetylene ligand, in the geometry found here, may well be a generally useful instrument for facilitating the formation of multiple bonds between transition metal atoms. Another structure illustrative of this possibility that is already in the literature[23] is that of $[(\eta^5\text{-}C_5H_5)(CO)Nb]_2(\mu\text{-}Ph_2C_2)_2$, where the counting of electrons and the shortness of the Nb-Nb distance (2.74 Å) suggest the existence of a double bond between the metal atoms. We intend to explore deliberately the possibility of using this concept to design and prepare new compounds containing multiple bonds between metal atoms.

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Supplementary Material Available: listings of the structure factor amplitudes for both structures (18 pages). Ordering information is given on any current masthead page.

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Molecular Structure and Bonding of a Silacyclopropane, Dimethyldispiro[bicyclo[4.1.0]heptane-7,2′-silacyclopropane-3′,7″-bicyclo[4.1.0]heptane]

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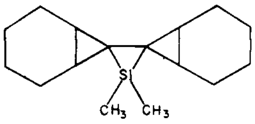
Abstract: The molecular structure of the first stable silacyclopropane compound has been determined and is compared with other three-membered ring compounds. CNDO calculations for C_2X heterocyclic ring systems demonstrate a decreasing C–X overlap population with increasing atomic number for a given periodic row. In addition, the enhanced stability associated with the dispiro structure in the silicon compound is confirmed as being due to increased C–X overlap population in the heteroring due to hyperconjugation bonding with the spiro cyclopropyl groups as previously suggested by Hoffmann. The compound exists with one cyclohexane ring folded towards the silicon atom and the other folded away. The silicon–ring carbon bond distance is 1.826 (3) Å and the carbon–carbon (heteroring) bond distance is 1.520 (3) Å. The structure of dimethyldispiro[bicyclo[4.1.0]heptane-7,2′-silacyclopropane-3,7″-bicyclo[4.1.0]heptane], $[(CH_3)_2Si(CC_6H_{10})_2]$, was determined from single-crystal x-ray data (2617 reflections) measured on a four-circle Picker x-ray diffractometer equipped with a graphite monochromator. The crystal system is triclinic with $a = 10.225$ (6) Å, $b = 14.680$ (9) Å, $c = 6.544$ (4) Å, $\alpha = 114.82$ (5)°, $\beta = 102.52$ (4)°, and $\gamma = 56.58$ (3)°, with two molecules per unit cell and $\rho_{\text{calcd}} = 1.098$ g cm^{-3}. Least-squares refinement gave a final agreement factor of $R_w = 0.071$ and $R = 0.092$.

Three-membered ring compounds which contain two carbon atoms and one heteroatom have been the subject of extensive investigations over many years. Oxiranes, thiiranes, and aziridines have been known for a long time and have a well-developed chemistry. Phosphiranes are of more recent vintage and are much less stable than their oxygen, sulfur, and nitrogen analogues.[2] After having been sought for at least 25 years by various research groups, the first silacyclopropanes were prepared in 1972.[3] Initially, the only such compounds which were available were those in which the silacyclopropane unit was part of a dispiro system, i.e., I, II, and III. More recently, hexamethylsilacyclopropane also could be prepared and isolated.[4] Compounds I, II, and III, however, were much more stable thermally than hexamethylsilacyclopropane.



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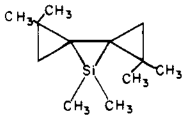

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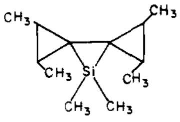
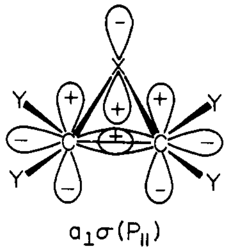
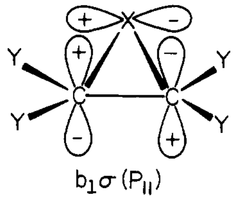


III

Structural studies have been carried out on oxiranes, thiiranes, aziridines, and phosphiranes. The C-C bond length in the C_2X ring has been found to vary with the stability of the $b_1\sigma$ molecular orbital[5] which has the symmetry indicated below. The donation of electrons from X into the anti-



$a_1\sigma(P_{\|})$
$(p_z - p_x, p_z)$



$b_1\sigma(P_{\|})$
$(p_x - p_z)$

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