Stereochemical Analysis of a Molecular Transition Metal "Hetero-Layered Sandwich" Complex, $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$, Containing a Nickel–Iron Bond: Steric Equivalence of the Ni(cyclobutadiene) Fragment with Iron Tricarbonyl and Fe(CO)(cyclobutadiene) Fragments

Earl F. Epstein[1] **and Lawrence F. Dahl**

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received July 7, 1969*

Abstract: A hetero-layered sandwich complex $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$, a product of the reaction between triirondodecacarbonyl and tetramethylcyclobutadienenickel dichloride, has been characterized from a single-crystal X-ray analysis. Its configuration consists of a nickel atom which is "sandwiched" between approximately coplanar cyclobutadiene and ferracyclopentadiene rings. The nickel(cyclobutadiene) fragment is coordinated to the five-membered ferracyclopentadiene ring both through a *cis*-butadiene–nickel interaction and through a nickel–iron electron pair bond of length 2.449 (3) Å. A detailed comparison of the structural features of this molecule is made with those of the related $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$ and $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2$-Fe(CO) molecules. It is shown that the disposition of the nickel(cyclobutadiene) fragment with respect to the ferracyclopentadiene ring is analogous to the similar orientations of the $Fe(CO)_3$ and Fe(CO)(cyclobutadiene) fragments relative to the ferracyclopentadiene rings in these other respective iron complexes. The compound forms crystals with four formula units in an orthorhombic cell of symmetry Pcam [nonstandard setting of Pbcm (D_{2h}^{11}, No. 57)] and of lattice parameters $a = 14.496 \pm 0.011$ Å, $b = 9.115 \pm 0.007$ Å, and $c = 14.520 \pm 0.011$ Å. Each molecule is required to have a crystallographic mirror plane of symmetry. Anisotropic–isotropic least-squares refinement has produced discrepancy factors of $R_1 = 6.5\%$ and $R_2 = 7.4\%$ based on 713 reflections obtained with an automated diffractometer.

The reaction between triirondodecacarbonyl and tetramethylcyclobutadienenickel dichloride yields in small amounts a compound which elemental analysis, molecular weight determination, and a mass spectrum indicated to be $(CH_3)_6C_8FeNi(CO)_3$.[2] Maitlis, Bruce, and Moseley,[2] who first carried out this reaction, found that an infrared spectrum of this product in CH_2Cl_2 solution showed two strong bands at 1920 cm^{-1} and 2000 cm^{-1} which are characteristic of terminal carbonyl frequencies.[3] The mass spectrum of this compound exhibited peaks at m/e 330 and m/e 216 which correspond to $(CH_3)_8C_8FeNi^+$ and $(CH_3)_8C_8^+$, respectively; however, no peaks were observed corresponding to either $(CH_3)_4C_4Fe^+$ (m/e 164) or $(CH_3)_4C_4^+$ (m/e 108). The fragmentation pattern was interpreted to indicate that the organic part of the molecule is not composed of two discrete $(CH_3)_4C_4$ species but instead is comprised of a $(CH_3)_8C_8$ unit. Nevertheless, a subsequent X-ray structural determination[4] of $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$,[5] which revealed a molecular configuration containing an Fe(CO) fragment bonded simultaneously to a ferracyclopentadiene system and to a cyclobutadiene part of the organic ligand, suggested an alternative model involving a ferracyclopentadiene system linked to a nickel(cyclobutadiene) residue. Hence, an X-ray determination of the structure of this organo(iron–nickel) compound was undertaken in order not only to ascertain its actual atomic arrangement and nature of bonding but also to obtain molecular parameters for comparison with those of related complexes.

Experimental Section

Data Collection. Crystals of the compound were generously supplied to us by Professor P. M. Maitlis of McMaster University. Many crystals of $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ have the shape of a distorted octahedron whose faces are the ⟨111⟩ form of the crystal. One such crystal, whose dimension was 0.14 mm along one side of the square plane of the distorted octahedron, was glued to the end of a glass fiber with the b axis along the fiber axis. The crystal in this orientation was mounted on a General Electric four-circle Datex-controlled automatic X-ray diffractometer equipped with a scintillation counter.

The crystal was first centered optically in the χ circle. The positions of a set of $h00$ reflections whose 2θ values ranged from 11.00 to 33.95° were determined and found to vary by no more than 0.02° in χ, indicating that the crystal was accurately aligned in the diffraction plane. The reciprocal lattice vector was made to lie in the plane of the χ circle for all reflections, by the adjustment of w, such that any pair of centrosymmetrically related reflections did not differ in ϕ when χ was changed by 180°. Thirty reflections were than carefully centered at a take-off angle of 2° (*i.e.*, the take-off angle at which data was collected). The angles which corresponded to these 30 reflections were used as input to program ANGSET,[6] in order not only to determine the crystallographic lattice param-

---

[1] This paper is based in part on a dissertation submitted by Earl F. Epstein to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree, Jan 1969.

[2] R. Bruce, K. Moseley, and P. M. Maitlis, *Can. J. Chem.*, **45**, 2011 (1967).

[3] R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 11 (1964).

[4] E. F. Epstein and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 493 (1970).

[5] H. W. Whitlock, Jr., and P. E. Sandvick, *ibid.*, **88**, 4525 (1966).

[6] ANGSET, a local modification of "Orientation and Angle Setting Generation Program," Program B-101, Argonne National Laboratory, 1965.

eters and their probable errors, but also to define the orientation of the crystal on the diffractometer. The least-squares procedure for the determination of the lattice parameters and their probable errors is available elsewhere.[7] These parameters should be regarded as instrumental lattice parameters, since they have been derived from the observed instrument angles which may be subject to systematic error.

The data were collected by the θ–2θ scan technique with Mo K$\bar{\alpha}$ radiation (λ 0.7107 Å), with a circular receiving aperture of 2-mm diameter at a distance of 31 mm from the crystal. Stationary-counter background counts were taken at each end of the scan for 20 sec. The scan, which was symmetric about the calculated value of 2θ, had a range of 2.0° for 2θ values which were less than 25°, and a range of 2.5° if 2θ were greater than 25°. The intensities of all diffracted beams from the symmetry-equivalent hkl, $\bar{h}kl$, and $h\bar{k}l$ octants with 2θ less than 40° were measured. The pulse height analyzer was adjusted to receive 90% of the diffracted intensity. The intensities of four standard reflections were measured periodically during the collection of data. No decay was discernible and no individual measurement of the intensity of a standard reflection differed from the average by more than 2%. No intensities were found which exceeded about 5000 counts/sec.

The conversion of the intensity data to observed structure factors and the assignment of standard deviations to each structure factor were obtained from the program DATRED.[7] Here the background is approximated by a straight line between the two measured background points. The standard deviation of the intensity is given by $\sigma^2(I) = C_T + t'^2C_B + EI^2$ where C_T and C_B are the total counts obtained in the scan and background measurements, t' represents the ratio of the total scan time to the total background time (t_s/t_B), and the intensity $I = (C_T - t'C_B)$. The last term in the expression for $\sigma^2(I)$ reflects our ignorance of any conditions which may cause variations in the intensities among equivalent reflections in an extinction-free, nonabsorbing crystal. Failure to include such a term has been shown to give excessively large weight to the more intense reflections.[8] The value of the constant E in the above equation was chosen arbitrarily as 0.0010. Each reflection for which the intensity I was less than $3\sigma(I)$ was considered to be unobserved. Lorentz polarization corrections were applied, and a set of observed structure factors was obtained. No anomalous dispersion or absorption corrections were made. For Mo K$\bar{\alpha}$ radiation, the values of the dispersion corrections to the atomic scattering factor for nickel are $\Delta f' = 0.4$ and $\Delta f'' = 1.2$.[9] Since the crystal possesses centrosymmetric space group symmetry, these very small dispersion corrections are presumed not to affect significantly the atomic coordinates in the compound.[10] The linear absorption coefficient for the compound is 12.9 cm^{-1} for Mo K$\bar{\alpha}$ radiation; for this value it was estimated that the maximum possible variation in the intensities caused by the neglect of absorption corrections is 9%. Standard deviations in the observed structure factors were assigned according to

$$\sigma^2(F_{hkl}) = [{}^1/_4LP][C_T + t'^2C_B)/(C_T - t'C_B)] + EF^2/4$$

The first term arises from counting statistics while the last term represents "instrument instability" or the above-mentioned "ignorance factor."

Program INTAV 3A[11] was used to merge the data from the three symmetry-equivalent octants. These data consisted of 650 contributors from the (+++) octant, 604 from the (+−+) octant, and 600 from the (−++) octant. The weighted discrepancy index was 1.9% for this merging, which yielded 713 independent, observed reflections.

Crystal Data. The compound $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ forms dark red crystals whose shape is often that of a flattened octahedron. Preliminary Weissenberg and precession photographs exhibited orthorhombic D_{2h}-2/m2/m2/m Laue symmetry and systematic absences of $\{0kl\}$ with l odd and $\{h0l\}$ with h odd. These extinctions indicate that the space group is either Pcam or the acentric group Pca2$_1$. Refinement of the structure was successful in the centrosymmetric group Pcam, which is the nonstandard labeling of the group Pbcm (D_{2h}^{11}, No. 57).[12] The lattice parameters and their errors, obtained by a least-squares procedure described elsewhere,[7] are $a = 14.496 \pm 0.011$, $b = 9.115 \pm 0.007$, and $c = 14.520 \pm 0.011$ Å. The cell volume is 1918 Å^3 and the total number of electrons, $F(000)$, in the unit cell is 504. Suspension of a crystal in trichloroethylene gave an experimental density of 1.45 ± 0.05 g/cm^3; for *four* molecules in the unit cell, the density is calculated to be 1.44 g/cm^3. Since the space group Pcam has an eightfold multiplicity of a general position, the four molecules in the unit cell must necessarily lie on crystallographic mirror planes at $z = \pm{}^1/_4$; hence, the nickel and iron atoms as well as the atoms of one carbonyl group each occupy a set of the following fourfold special positions (4d): $\pm\,(x, y, {}^1/_4;\ {}^1/_2 + x, \bar{y}, {}^1/_4)$. The ten remaining independent nonhydrogen atoms each occupy a set of the following eightfold general positions (8e): $\pm(x, y, z;\ \bar{x}, \bar{y}, {}^1/_2 + z;\ x, {}^1/_2 - y, \bar{z};\ \bar{x}, {}^1/_2 + y, {}^1/_2 - z)$. Therefore, the solution of the structure required the location of one iron, one nickel, ten carbon, two oxygen, and, ideally, twelve hydrogen atoms.

Solution of the Structure

An unsharpened, three-dimensional Patterson function,[13] based on the corrected intensities, gave more than the number of large peaks which were expected on the basis of the symmetry Pcam. Nevertheless, the assumption that the metal atoms were separated by about 2.5 Å led to a self-consistent interpretation of most of these vector positions in terms of initial coordinates for the iron and nickel atoms. From three successive Fourier syntheses the approximate positions were obtained for all other nonhydrogen atoms. These coordinates were refined by isotropic full-matrix least squares[14] based on the minimization of $\Sigma w_i \Delta F_i^2$, where $w_i = 1/\sigma_i^2$. The atomic scattering factors of Hanson, *et al.*,[15] were used in all structure factor calculations. After that cycle in which the shifts in positional and thermal parameters were less than 0.5 of their respective errors, the values of the discrepancy factors were $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100 = 7.6\%$ and $R_2 = [\Sigma w \cdot (|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} \times 100 = 8.5\%$. The isotropic thermal parameters of 3.6 Å^2 for iron and 2.6 Å^2 for nickel were then converted to anisotropic form; two more cycles of anisotropic–isotropic least-squares refinement lowered the discrepancy factors to their final values of 6.5% and 7.4%. A three-dimensional difference Fourier synthesis based on the parameters from the final least-squares cycle revealed no electron density greater than 0.5 e/Å^3.

From the final anisotropic thermal parameters for the iron and nickel atoms, root-mean-square amplitudes of vibration along the three principal axes of the thermal ellipsoid were computed[16] for each atom. For the nickel atom these values are 0.17, 0.19, and 0.19 Å; for the iron atom the values are 0.18, 0.21, and 0.25 Å, thereby indicating relatively small anisotropic motion for these atoms. The coordinates of the iron and nickel atoms obtained from the final mixed anisotropic–isotropic cycle of refinement were then exchanged, and isotropic thermal parameters for these

---

(7) E. F. Epstein, Ph.D. Thesis, University of Wisconsin, Madison, Wisconsin, Jan 1969.

(8) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(9) D. H. Templeton in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 215.

(10) D. H. Templeton, *Acta Cryst.*, **8**, 842 (1955).

(11) P. W. Sutton and M. D. Glick, "A Crystallographic Data Correlation Program for the CDC 1604," University of Wisconsin, 1964.

(12) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p 145.

(13) All Patterson and Fourier syntheses were carried out with the Blount program: J. F. Blount, Ph.D. Thesis, University of Wisconsin, 1965.

(14) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1962.

(15) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, **17**, 1040 (1964).

(16) C. K. Johnson, "ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," ORNL-3794, Oak Ridge National Laboratory, 1965.

atoms were varied for two additional cycles of least-squares refinement with all other parameters fixed; the isotropic thermal parameters for the iron and nickel atoms diverged to 1.8 and 4.6 Å^2, respectively, and the discrepancy factors increased to $R_1 = 8.5\%$ and $R_2 = 9.5\%$. The much greater difference between the isotropic thermal parameters of the two metal atoms and the increase (by 1%) of the corresponding isotropic discrepancy factors supported the initial assignments of the relative positions of the iron and nickel atoms made unambiguously on the basis of chemical considerations.

The coordinates and thermal parameters as obtained from the output of the final anisotropic–isotropic least-squares cycle appear in Table I.[17] Atomic distances and angles in the molecule are presented in Table II along with estimated standard deviations which contain the effect of errors in the lattice parameters as calculated by the Busing-Martin-Levy program.[18] The equations of planes which were fitted to various sets of atoms by a least-squares procedure[19] and the perpendicular displacements of atoms from these planes are given in Table III.

Table I. Final Atomic Parameters with Their Standard Deviations from Rigid-Body Least-Squares Refinement for $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$

	x ($10^4\sigma_x$)	y ($10^4\sigma_y$)	z ($10^4\sigma_z$)	B ($10\sigma_B$)
Ni	0.4926 (1)	0.2643 (2)	0.7500	*a*
Fe	0.3367 (2)	0.1607 (3)	0.7500	*a*
O(1)	0.3233 (7)	−0.0674 (11)	0.6090 (8)	8.5 (3)
O(2)	0.1561 (10)	0.2894 (15)	0.7500	7.6 (4)
C(1)	0.3294 (10)	0.0270 (16)	0.6657 (11)	7.0 (4)
C(2)	0.2288 (14)	0.2318 (21)	0.7500	6.1 (5)
C(3)	0.3846 (7)	0.3042 (11)	0.6611 (8)	3.6 (3)
C(4)	0.4136 (7)	0.4396 (11)	0.7021 (8)	3.8 (3)
C(5)	0.5824 (7)	0.1189 (12)	0.6987 (8)	3.6 (3)
C(6)	0.6234 (7)	0.2685 (12)	0.7005 (7)	3.6 (3)
C(7)	0.3806 (9)	0.2894 (14)	0.5578 (10)	6.0 (3)
C(8)	0.4454 (9)	0.5761 (13)	0.6463 (10)	5.4 (3)
C(9)	0.5678 (8)	0.0059 (13)	0.6250 (9)	5.0 (3)
C(10)	0.6620 (9)	0.3620 (14)	0.6262 (9)	5.6 (3)

[a] Anisotropic temperature factors for the metals were used with the form $\exp\{-[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]\}$. For these atoms in special positions on mirror planes, the thermal coefficients B_{13} and B_{23} are required by symmetry to be zero. The resulting thermal coefficients (with standard deviations of the last significant figure given in parentheses) were

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0.0028 (1)	0.0084 (3)	0.0033 (1)	0.0001 (1)	0	0
Fe	0.0035 (1)	0.0093 (4)	0.0060 (2)	−0.0007 (2)	0	0

The corresponding root-mean-square amplitudes of vibration (Å) along the principal axes of the thermal ellipsoids are

	r_1	r_2	r_3
Ni	0.172	0.188	0.189
Fe	0.181	0.207	0.254

Table II. Distances and Angles with Standard Deviations[a,b]

A. Bonding Intramolecular Distances, Å

Metal–metal bond	Fe–Ni	2.449 (3)
Iron–(carbonyl carbon) bonds	Fe–C(1)	1.730 (16)
	Fe–C(2)	1.693 (21)
Ferracyclopentadiene bonds	Fe–C(3)	1.965 (11)
	C(3)–C(4)	1.433 (13)
	C(4)–C(4′)	1.390 (23)
Nickel–(ring carbon) bonds	Cyclobutadiene	
	Ni–C(5)	2.002 (11)
	Ni–C(6)	2.029 (10)
		2.016 (av)
	Ni–centroid	1.724
	Ferracyclopentadiene	
	Ni–C(3)	2.061 (11)
	Ni–C(4)	2.084 (11)
		2.072 (av)
	Ni–[centroid of butadiene fragment]	1.672
Cyclobutadiene bonds	C(5)–C(6)	1.488 (14)
	C(5)–C(5′)	1.489 (23)
	C(6)–C(6′)	1.437 (22)
		1.463 (av)
Carbonyl bonds	C(1)–O(1)	1.194 (15)
	C(2)–O(2)	1.178 (20)
		1.186 (av)
(Ferracyclopentadiene carbon)–(methyl carbon) bonds		
	C(4)–C(8)	1.556 (15)
	C(3)–C(7)	1.507 (18)
(Cyclobutadiene carbon)–(methyl carbon) bonds		
	C(5)–C(9)	1.500 (15)
	C(6)–C(10)	1.484 (15)

B. Intramolecular Angles, Deg

Angles centered on iron			
C(1)–Fe–C(2)	102.3 (7)	Ni–Fe–C(1)	109.2 (6)
C(2)–Fe–C(3)	94.1 (6)	Ni–Fe–C(2)	134.8 (6)
C(1)–Fe–C(1′)	90.1 (10)	Ni–Fe–C(3)	54.3 (6)
C(3)–Fe–C(3′)	82.1 (7)	Ni–Fe–C(4)	45.4 (6)
Angles centered on nickel			
C(3)–Ni–C(4)	40.4 (4)	C(5)–Ni–C(6)	43.3 (4)
C(4)–Ni–C(4′)	38.9 (7)	C(6)–Ni–C(6′)	41.4 (7)
C(3)–Ni–C(3′)	77.6 (7)	C(5)–Ni–C(5′)	43.7 (6)
Fe–Ni–C(5)	110.1 (6)	Fe–Ni–C(6)	150.4 (6)
Carbonyl angles			
Fe–C(1)–O(1)	178.4 (13)	Fe–C(2)–O(2)	176.0 (18)
Ferracyclopentadiene angles			
C(3)–Fe–C(3′)	82.1 (7)	C(7)–C(3)–C(4)	120.2 (10)
Fe–C(3)–C(4)	113.8 (8)	C(8)–C(4)–C(3)	124.0 (10)
C(3)–C(4)–C(4′)	114.6 (7)	C(8)–C(4)–C(4′)	121.4 (10)
C(7)–C(3)–Fe	125.5 (8)		
Cyclobutadiene angles			
C(9)–C(5)–C(5′)	135.5 (6)	C(5)–C(6)–C(6′)	91.0 (6)
C(9)–C(5)–C(6)	134.3 (6)	C(5′)–C(5)–C(6)	89.0 (6)
C(10)–C(6)–C(5)	131.6 (6)		
C(10)–C(6)–C(6′)	136.6 (7)		

C. Intramolecular Nonbonding Distances, Å

Ferracyclopentadiene distances		Iron–carbonyl oxygen distances	
C(3)···C(3′)	2.58 (2)	Fe···O(1)	2.92 (1)
C(7)···C(8)	3.06 (2)	Fe···O(2)	2.87 (2)
C(8)···C(8′)	3.01 (3)		
C(2)···C(3)	2.68 (2)		
Cyclobutadiene distances		Carbonyl carbon distances	
C(9)···C(10)	3.52 (2)	C(1)···C(1′)	2.45 (3)
C(9)···C(9′)	3.63 (3)	C(1)···C(2)	2.67 (2)
C(10)···C(10′)	3.60 (3)		

[a] Standard deviations of last significant figures are given in parentheses. [b] Those atoms which are related by the crystallographic mirror plane are designated by C(*n*) and C(*n*′).

Discussion

Description of the Structure. The molecular structure of $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ as shown in Figure 1 is that of a nickel atom which is "sand-

---

(17) Calculated and observed structure factors utilized in the least-squares refinement are deposited as Document No. NAPS-00773 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York N. Y. 10022. A copy may be secured by citing the document number and remitting \$1.00 for microfiche or \$3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

(18) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, 1964.

(19) D. L. Smith, Ph.D. Thesis, University of Wisconsin, 1962.

Table III

A. Equations of Planes and Distances (Å) from these Planes[a]

(a) Plane containing C(3), C(4), C(3′), and C(4′)

$0.9468X - 0.3219Y - 0.0Z - 4.3861 = 0$

Fe	−0.237	C(2)	−1.925
Ni	1.599	C(7)	0.037
C(1)	0.055	C(8)	−0.011
O(1)	0.249		

(b) Plane containing C(1), C(3), C(1′), and C(3′)

$0.9533X - 0.3022Y + 0.0Z - 4.4773 = 0$

Fe	−0.267	C(4)	0.027
Ni	1.602	C(7)	−0.014
O(1)	0.176	C(8)	0.092
C(2)	−1.952		

(c) Plane containing C(5), C(6), C(5′), and C(6′)

$0.9164X - 0.4002Y + 0.0Z - 7.3033 = 0$

Fe	−3.416	C(1)	−3.026
Ni	−1.724	C(3)	−3.303
C(9)	0.218	C(4)	−3.412
C(10)	0.170		

(d) Plane containing C(7), C(8), C(7′), and C(8′)

$0.9410X - 0.3384Y + 0.0Z - 4.2996 = 0$

C(3)	0.009	Fe	−0.202
C(4)	−0.014	Ni	1.604

(e) Plane containing C(9), C(10), C(9′), and C(10′)

$0.9218X - 0.3876Y + 0.0Z - 7.5663 = 0$

C(5)	−0.204	Fe	−3.635
C(6)	−0.184	Ni	−1.918

B. Angles (deg) between the Normals to Planes

a–b	1	*c–d*	4
a–c	5	*c–e*	1
a–d	1	*d–e*	3
a–e	4		
b–c	6		
b–d	2		
b–e	5		

C. Angles between Interatomic Vectors and the Normals to Planes

Vector	Plane	Angle, deg
Fe–Ni	*a*	41
Fe–Ni	*c*	46
C(3)–C(7)	*a*	90
C(4)–C(8)	*a*	91
C(5)–C(9)	*c*	98
C(6)–C(10)	*c*	97
Fe–C(2)	*a*	4
Fe–C(2)	*b*	5
Ni–C(3)	*a*	39
Ni–C(4)	*a*	40
Ni–C(5)	*c*	31
Ni–C(6)	*c*	32
Ni–(centroid of the butadiene fragment)	*a*	17
Ni–(centroid of the butadiene fragment)	*c*	2

[a] The equations of the planes and the distances were obtained from the Smith plane program.[19] Unit weights were used for all atoms in the calculations. The equation of the plane is expressed in orthogonal coordinates X, Y, Z which are related to the crystallographic fractional coordinates x, y, z by the transformation: $X = ax$, $Y = by$, and $Z = cz$.

wiched" between approximately coplanar cyclobutadiene and ferracyclopentadiene rings. Each molecule is crystallographically required to have a mirror plane of symmetry, which passes through the nickel and iron atoms as well as one carbonyl group, and relates all other corresponding pairs of atoms to each other. The coordination between the nickel atom and the ferracyclopentadiene ring involves both a *cis*-butadiene–nickel interaction and a nickel–iron single bond linkage.

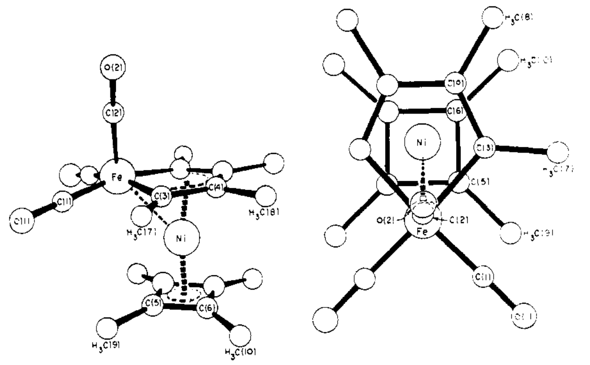

Figure 1. The molecular configuration of $[Fe(CO)_3(CH_3C_2CH_3)_2]$-$Ni[C_4(CH_3)_4]$.

The iron atom contained in the ferracyclopentadiene ring has a square-pyramidal-like arrangement of carbon atom ligands which includes the two terminal diene carbon atoms of the *cis*-butadiene portion of the ring and the carbon atoms of the three terminal carbonyl groups. The iron atom is displaced from the exact basal plane of four carbon atoms by 0.26 Å toward the apical carbonyl carbon atom. A sixth coordination site is inhabited by the nickel atom. The environment about the nickel atom can be formally considered as five-coordinate with two sites occupied by the cyclobutadiene ring, two sites occupied by the *cis*-butadiene portion of the ferracyclopentadiene ring, and the fifth site filled by the iron atom. Figure 2 shows the arrangement of the molecules in the orthorhombic cell. The fact that the shortest *intermolecular* contacts are 3.5 Å (Table II) supports the premise that packing forces are not important in the determination of the overall geometry of $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$.

The Ferracyclopentadiene Ring. The ferracyclopentadiene ring in $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ is common to the compounds $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$,[20] $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$,[4] $Fe(CO)_3(C_6H_4CHCC_6H_5)Fe(CO)_3$,[21] $Fe_3(CO)_{10}(C_2H_2)_5$,[22] and the black isomer of $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$.[23] Metallocyclopentadiene rings involving other transition metals have also been structurally characterized for the molecular compounds $Os(CO)_3(HC_2CH_3)_2Os(CO)_3$[24] and $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$.[25] The molecular parameters of the ferracyclopentadiene ring in $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ do not differ appreciably from those of this ring in any of the above known structures. The carbon–carbon distances follow the usual trend for a *cis*-butadiene system bonded to a transition metal. The iron–carbon σ bond distance, Fe(1)–C(3), of 1.96 Å agrees well with the corresponding values of 1.94 and 1.95 Å in $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$ and of 1.98 and 1.99 Å in $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$. The methyl substituents of the five-membered ferracyclopentadiene ring essentially lie in the plane of the *cis*-butadiene fragment,

---

(20) A. A. Hock and O. S. Mills, *Acta Cryst.*, **14**, 139 (1961).

(21) P. Y. Degrève, J. Meunier-Piret, M. Van Meerssche, and P. Piret, *ibid.*, **23**, 119 (1967).

(22) C. E. Strouse and L. F. Dahl, submitted for publication.

(23) R. P. Dodge and V. Schomaker, *J. Organometal. Chem.*, **3**, 274 (1965).

(24) R. P. Dodge, O. S. Mills, and V. Schomaker, *Proc. Chem. Soc.*, 380 (1963).

(25) L. R. Bateman and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 7292 (1969).

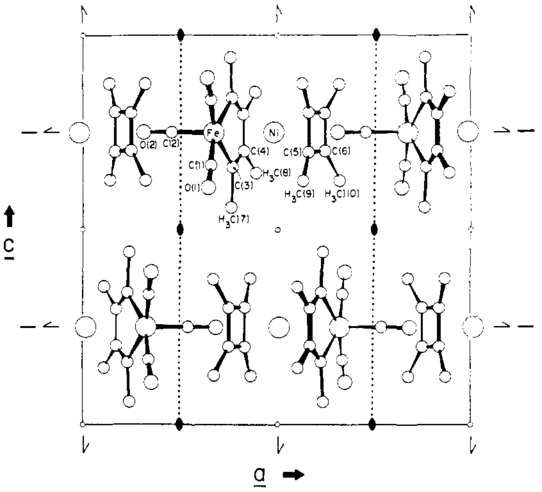

Figure 2. [010] projection of the orthorhombic unit cell showing the orientations of the four $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ molecules lying on the crystallographic mirror planes.

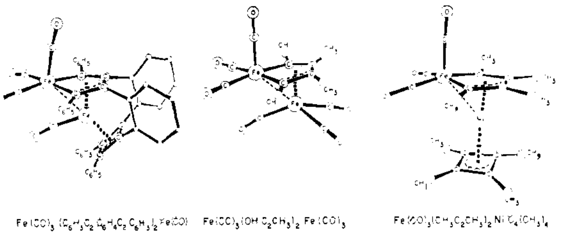

Figure 3. Comparison of the molecular geometries of $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$, $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$, and $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ showing the coordination of the common ferracyclopentadiene ring to the electronically- and sterically-equivalent $Fe(CO)_3$, Fe(CO)(cyclobutadiene), and Ni(cyclobutadiene) fragments.

with the perpendicular displacements for C(7) and C-(8) being only 0.04 Å and 0.01 Å, respectively. This nearly planar configuration possessed by the *cis*-butadiene fragment and its methyl carbon substituents supports the view of an olefinic-like character for all of the diene carbon atoms. The perpendicular displacement of the iron atom by 0.26 Å from the exact basal carbon plane, comprised of atoms C(1) and C(3) and their mirror-plane related atoms C(1′) and C(3′), is analogous to the displacement of the iron atom from the mean basal carbon plane by 0.18 Å in $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$ and by 0.11 Å in $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$.

Structural Comparison of $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ with $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ and $Fe(HOC_2CH_3)_2Fe(CO)_3$: Steric Equivalence of the Ni(cyclobutadiene), Fe(CO)(cyclobutadiene), and $Fe(CO)_3$ Fragments. The structural data available for the $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$, $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$, and $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ molecules (depicted in Figure 3) make possible a detailed comparison of the effect on the geometry of the common ferracyclopentadiene ring, due to the coordination of the electronically equivalent $Fe(CO)_3$, Fe(CO)(cyclobutadiene), and Ni(cyclobutadiene) fragments. In $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$ the ferracyclopentadiene ring is bonded to an iron tricarbonyl fragment whose localized trigonal axis is approximately perpendicular to the plane of the five-membered ring, while in $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ the ferracyclopentadiene linkage is to a Fe(CO)(cyclobutadiene) moiety. A comparison of the molecular geometries of these two compounds demonstrates the steric equivalence between a cyclobutadiene ring and two carbonyl groups, since the formal replacement of one with the other occurs without an appreciable alteration of the geometry of the remaining portion of the molecule.[4] The disposition of the cyclobutadiene ring is consistent with that of the two formally replaced carbonyl groups in that the line from the cyclobutadiene-coordinated iron atom to the centroid of the cyclobutadiene ring forms bond angles with adjacent atoms which are remarkably similar to the angles formed by the line from the nonring iron atom to the centroid of the two carbonyl groups.[4] The cyclobutadiene ring in $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ is inclined such that the dihedral angle between the four- and five-membered planes is 47°. The formal substitution of a Ni(cyclobutadiene) fragment in place of an iron tricarbonyl group or an Fe(CO)(cyclobutadiene) residue leads to a configuration in which the cyclobutadiene and ferracyclopentadiene rings are coplanar to within 5°. Hence, this configuration with the localized fourfold axis of the idealized Ni(cyclobutadiene) moiety approximately perpendicular to the mean plane of the *cis*-butadiene portion of the ferracyclopentadiene ring is analogous to that of $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$, with the localized threefold axis of the $Fe(CO)_3$ group approximately perpendicular to the five-membered ring (see Figure 3). The coplanarity of the cyclobutadiene and ferracyclopentadiene rings in $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$, as opposed to the 47° formed by the normals of these planes in $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ when a carbonyl group is also coordinated to the nonring metal atom, emphasizes that their molecular geometries are apparently determined primarily by the steric activity of the substituents bonded to the nonring metal atom.

The (Ferracyclopentadiene Ring)–Nickel(cyclobutadiene) Interaction. The nickel atom in $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ is symmetrically placed with respect to the diene carbon fragment of the ferracyclopentadiene ring. The two independent nickel to diene carbon distances of 2.06 and 2.08 Å are slightly longer than the nickel to cyclobutadiene carbon distances of 2.00 and 2.03 Å. With due allowance made for the smaller covalent radius of nickel (*viz.*, 1.149 Å for nickel *vs.* 1.165 Å for iron), the nickel–iron distance of 2.45 Å compares favorably with the iron–iron electron pair distances in $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$ (2.49 Å),[20] $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ (2.49 Å),[4] $Fe(CO)_3(C_6H_4CHCC_6H_5)Fe(CO)_3$ (2.52 Å),[21] $Fe_3(CO)_{10}(C_2H_2)_5$ (2.49 Å),[22] and $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$ (2.43 and 2.44 Å).[23]

The structure of $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ makes possible an assessment of the effect of the weak interaction of one carbonyl group from each nonring iron tricarbonyl fragment in $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$, $Fe(CO)_3(C_6H_4CHCC_6H_5)Fe(CO)_3$, $Fe_3(CO)_{10}(C_2H_2)_5$, and $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$, and from the Fe(CO)(cyclobutadiene) fragment in $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$, with the ferracyclopentadiene iron atom in each of these complexes. The formal replacement of an $Fe(CO)_3$ fragment or an Fe(CO)(cyclobutadiene) fragment by the electronically equivalent nickel(cyclobutadiene) residue, which thereby amounts to the removal of the weakly interacting carbonyl group, has produced little change in the geometries of these ferracyclopentadiene–metalloorganic systems. This relative insensitivity to the presence of a weakly bridging carbonyl group (which is not surprising) clearly shows that the overall configurations of these compounds are dominated by a combination of the *cis*-butadiene bonding with the metal atom[26] and the metal–metal electron-pair bond. The primary importance of these two interactions in stabilizing the entire complex is substantiated by the fact that the basic molecular geometry of the structurally related osmium analog, $Os(CO)_3(HC_2CH_3)_2Os(CO)_3$,[24] does not possess the weakly bridging carbonyl group in that the nonring $Os(CO)_3$ fragment is rotated by approximately 60° about its localized threefold axis relative to the osmacyclopentadiene ring.

The Cyclobutadiene Ring. The crystal structures of several compounds involving a transition metal bonded to a cyclobutadiene ring have been previously reported.[4,27–29] One of these compounds, $[Ni\{C_4(CH_3)_4\}Cl_2]_2 \cdot C_6H_6$,[27] also contains a nickel(tetramethylcyclobutadiene) residue. The nickel to cyclobutadiene carbon distances of 2.00, 2.01, 2.03, and 2.05 Å are in good agreement with those of 2.00 and 2.03 Å in $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$. The methyl carbon atoms are displaced from the plane of the cyclobutadiene ring away from the nickel atom by an average value of 0.19 Å in $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ compared to an average value of 0.17 Å in $[Ni\{C_4(CH_3)_4\}Cl_2] \cdot C_6H_6$. Kettle[30] has interpreted the bending of these methyl substituents out of the plane of the cyclobutadiene carbon ring as resulting from interactions between the metal orbitals and the σ framework of the ring system; he estimated for $[Ni\{C_4(CH_3)_4\}Cl_2] \cdot C_6H_6$ that the ratio of σ to π contributions to the nickel–cyclobutadiene interaction is 1:1.

In $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ there is marginal evidence that the cyclobutadiene ring deviates somewhat from a square arrangement in that two of the three independent C–C bond distances are 1.49 Å, while the third one is 1.44 Å. The weighted average C–C distance of 1.47 Å is near to the average C–C distance of 1.44 Å in $[Ni\{C_4(CH_3)_4\}Cl_2] \cdot C_6H_6$,[26] 1.46 Å in $Fe(CO)_3\{C_4(C_6H_5)_4\}$,[28] and 1.45 Å in $Mo(CO)_3P(C_6H_5)_3(C_4H_4)$.[29] It is noteworthy that the indicated distortion of the cyclobutadiene ring in $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ can be rationalized theoretically in terms of a molecular orbital model of the kind first invoked (without any experimental knowledge of such a linkage) by Longuet-Higgins and Orgel[31] to account for the stability of the cyclobutadiene molecule when coordinated to a transition metal complex. Their bonding model involving a square-planar cyclobutadiene molecule assumed that the local geometry of the metal–cyclobutadiene system has C_{4v}-4mm symmetry, such as to preserve the doubly-degenerate cyclobutadiene orbitals in their interactions with the appropriate metal orbitals. The orbital degeneracy of such a system is unaffected in such a molecular complex as $Fe(CO)_3\{C_4(C_6H_5)_4\}$, where the localized threefold axis of the iron tricarbonyl fragment is coincident with the localized fourfold axis of the iron(cyclobutadiene) system. However, the reduction in the localized symmetry from C_{3v}-3m to C_s-m when a ferracyclopentadiene ligand is formally substituted in place of the three carbonyl groups, such as occurs in the $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ molecule, would result in a breakdown of the cylindrical degeneracy of the metal orbitals which in turn would remove the degeneracy of the doubly-degenerate cyclobutadiene orbitals. These symmetry arguments which qualitatively predict a resulting nonuniformity of electron density about the cyclobutadiene ring might be responsible for the observed indication of such a deformation in the cyclobutadiene ring of the $[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$ molecule.

Acknowledgments. We wish to express our appreciation to Professor Peter M. Maitlis of McMaster University for furnishing us with a sample of the compound, and for his interest in our structural characterization. We thank the Air Force Office of Scientific Research for generous financial sponsorship of this work (AFOSR 518-66). E. F. E. appreciatively acknowledges the predoctoral fellowship of the National Institutes of Health for the academic year 1967–1968. This research was made possible through extensive utilization of the CDC 1604 and 3600 computers at the University of Wisconsin Computing Center, and we are especially indebted for the financial support of these computers from NSF and WARF, made available through the University Research Committee.

(26) M. R. Churchill and R. Mason, *Advan. Organometal. Chem.*, **5**, 93 (1967), and references contained therein.

(27) J. D. Dunitz, H. C. Mez, O. S. Mills, and H. Schearer, *Helv. Chim. Acta*, **45**, 647 (1962).

(28) R. P. Dodge and V. Schomaker, *Acta Cryst.*, **18**, 614 (1965).

(29) R. E. Davis, Abstracts of Papers, National Meeting of the American Crystallographic Association, Minneapolis, Minn., Aug 1967, p 95; R. E. Davis, private communication to L. F. Dahl, Sept 1968.

(30) S. F. A. Kettle, *Inorg. Chim. Acta*, **1**, 303 (1967).

(31) H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).