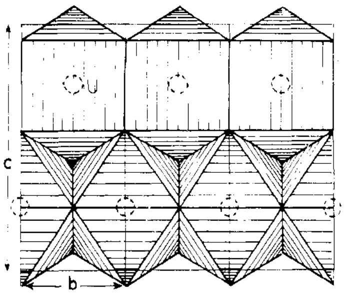

Figure 4. The sheet structure of UI_3, formed when adjacent UI_4 chains fuse and liberate one terminal iodine atom per octahedron.

distances are not much shorter than the sum of the ionic radii of U^{4+} and $I^- = 3.16$ Å. The bond angles in the octahedra are consistent with the uranium repulsions.

UI_4 is converted by gentle heating into UI_3. Presumably the layers of UI_4 chains at $x = 0$ and $x = {}^1/_2$ then become the sheets of the UI_3 structure shown in Figure 4. It is likely that in the conversion one of the two terminal iodine atoms in every octahedron is liberated, adjacent chains fuse, and cross-linked, linear –U–U–U– chains are formed with the same U–U separation as in UI_4. The U coordination polyhedron changes from an octahedron to a bicapped trigonal prism.

The structures of the actinide halides have been reviewed recently,[8] and UI_4 is the only actinide tetrahalide to show a chain structure ($UI_2I_{4/2}$). However, the chain structure, either linear with trans terminal halide atoms or zigzag with cis terminal atoms, is common in the transition-metal tetrahalides. Although none of these are isostructural with UI_4. Zigzag chains are found in $ZrCl_4$ and $HfCl_4$,[9] $TcCl_4$,[10] $PtCl_4$, $PtBr_4$, and α-PtI_4[11] and linear chains in $NbCl_4$,[12] α-$MoCl_4$,[13] $OsCl_4$,[14] and α-NbI_4.[15] The zigzag chain is found where there is no metal-metal attraction, while the linear chain generally signifies a metal-metal interaction. An unusual chain (corner-linked bioctahedra Re_2Cl_9) is found in $ReCl_4$.[16] TeI_4 shows a Te_4I_{16} tetramer.[17] UI_4 is thus a new variant of the infinite-chain structure $MX_2X_{4/2}$, previously found only in the halides of the transition metals.

Registry No. UI_4, 13470-22-9.

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(8) J. C. Taylor, *Coord. Chem. Rev.*, **20**, 197 (1976).
(9) B. Krebs, *Angew. Chem., Int. Ed. Engl.*, **8**, 146 (1969).
(10) M. Elder and B. R. Penfold, *Inorg. Chem.*, **5**, 1197 (1966).
(11) M. F. Pilbrow, *J. Chem. Soc., Chem. Commun.*, 270 (1972).
(12) D. R. Taylor, J. C. Calabrese, and E. M. Larsen, *Inorg. Chem.*, **16**, 721 (1977).
(13) D. L. Kepert and R. Mandyczewsky, *Inorg. Chem.*, **7**, 2091 (1968).
(14) F. A. Cotton and C. E. Rice, *Inorg. Chem.*, **16**, 1865 (1977).
(15) L. F. Dahl and D. L. Wampler, *Acta Crystallogr.*, **15**, 903 (1962).
(16) F. A. Cotton, B. G. De Boer, and Z. Mester, *J. Am. Chem. Soc.*, **95**, 1159 (1973).
(17) V. Paulat and B. Krebs, *Angew. Chem., Int. Ed. Engl.*, **15**, 39 (1976).

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Crystal Structure at –35 °C of (Cyclobutadiene)(1,2-bis(diphenylphosphino)ethane-*P*,*P*′)iron Carbonyl and an Examination of Stereochemical Distortions in Cyclobutadiene–ML_3 Complexes

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The structure of $(C_4H_4)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Fe(CO)$ has been determined by single-crystal X-ray diffraction techniques with three-dimensional data gathered at –35 °C by counter methods. Yellow, platelike single crystals form in triclinic space group $P\bar{1}$ with unit cell constants at –35 °C $a = 9.608$ (8) Å, $b = 14.694$ (3) Å, $c = 9.473$ (2) Å, $\alpha = 103.30$ (1)°, $\beta = 102.54$ (2)°, and $\gamma = 92.73$ (2)°. The calculated density of 1.414 (4) g cm^{-3} for two molecules per unit cell of the complex agrees with the measured value of 1.45 g cm^{-3}. Full-matrix least-squares refinement of the structure has converged with an R index (on $|F|$) of 0.049 for the 4890 symmetry-independent reflections within the Mo Kα shell defined by $4 < 2\theta < 55°$ which have $I_o/\sigma(I_o) > 2$. The iron atom is bonded to the cyclobutadiene ring in a symmetric manner, to the two phosphorus atoms of the diphosphine ligand, and to the CO ligand. As a consequence of the electron-donating capacity of the diphosphine ligand, the electron-withdrawing CO group is more firmly bound to Fe than in the corresponding $Fe(CO)_3$ complex, as indicated by the Fe–C and C–O bond lengths (1.742 (3) and 1.165 (4) Å) and by the lower frequency of the CO symmetric stretch (1880 cm^{-1}), as compared to the values for the $Fe(CO)_3$ complex. Stereochemical results for ten cyclobutadiene–transition-metal complexes of the form $(C_4R_4)ML_3$, which have been characterized by X-ray diffraction methods, have been analyzed in terms of distortions from two idealized symmetrical structures, one in which an M–L bond eclipses a ring carbon atom and one in which an M–L bond bisects a ring C–C bond. The observation that torsion parameters for these structures are distributed over the entire range between those of the two idealized structures supports the experimental results and theoretical suggestions of a low barrier in such complexes.

Introduction

As part of an investigation in our laboratory of the structural and spectroscopic consequences of the systematic substitution of phosphine ligands in metal complexes of the form $[(\pi\text{-}C_nH_n)Fe(PR_3)_m(CO)_{3-m}]^{p+}$ ($n = 4$ or 5, $m = 0$–2, $p = 0$ or 1), we have determined the crystal structure of $(C_4H_4)Fe(P(C_6H_5)_2CH_2\text{–})_2(CO)$, a species obtained by photolysis of the parent tricarbonyl complex in the presence of $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$.[1] This structural study also affords an examination of the geometry of an unsubstituted cyclobutadiene ligand for which only a few examples have been reported[2–4] and for which a very low barrier of rotation about the metal–C_4 axis has been predicted by Hoffmann and co-workers.[5]

In addition to reporting the details of this crystal structure, this paper provides the opportunity for an assessment of the

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(1) Slegeir, W.; Pettit, R., unpublished results.
(2) Davis, M. I.; Speed, C. S. *J. Organomet. Chem.* **1970**, *21*, 401.
(3) Riley, P. E.; Davis, R. E. *J. Organomet. Chem.* **1976**, *113*, 157.
(4) Riley, P. E.; Davis, R. E. *J. Organomet. Chem.* **1977**, *137*, 91.
(5) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546.

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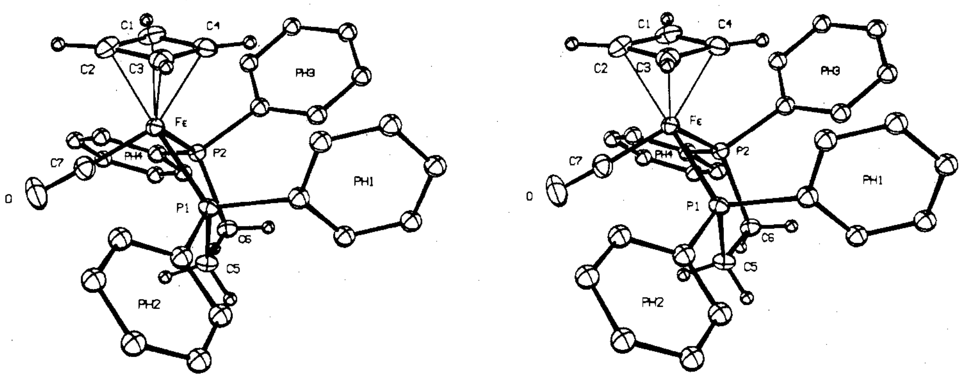

Figure 1. Stereoscopic view of the $(C_4H_4)Fe(dppe)(CO)$ molecule, illustrating the atom numbering scheme. Nonhydrogen atoms are shown as ellipsoids (or spheres) of 30% probability and hydrogen atoms as spheres of radius 0.1 Å.

stereochemical distortions of complexes of the form (C_4R_4)-ML_3 from the idealized symmetrical structures **1** (eclipsed) and **2** (staggered) for the crystallographically characterized cyclobutadiene–metal complexes. (L_3 represents an assortment of ligands which are not necessarily equivalent; e.g., $L_1 = L_2 = CO$, $L_3 = P(C_6H_5)_3$.) These evaluations corroborate the predictions of Hoffman et al.

1

2

Experimental Section

A sample of $(C_4H_4)Fe(dppe)(CO)$, where dppe represents $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$, was provided by Professor Rowland Pettit. Slow evaporation (ca. 5 days) of an acetone solution yielded excellent yellow, platelike single crystals. A well-formed specimen was attached to a glass fiber and transferred to a Syntex $P2_1$ automated diffractometer where it was maintained in a stream of cold (−35 °C), dry nitrogen during the course of all crystallographic experiments. Preliminary examination of the crystal with the diffractometer indicated symmetry no higher than that of the triclinic system (space group $P1$ (No. 1) or $P\bar{1}$ (No. 2)). Crystal data and data collection details are summarized in Table I. The recorded X-ray intensities were reduced, corrected for absorption, and assigned standard deviations (with $p = 0.02$) as described elsewhere.[6]

Solution and Refinement of the Crystal Structure

The structure was solved by standard heavy-atom procedures and refined by full-matrix least-squares methods.[7] The function minimized in refinement is $\sum w(|F_o| - |F_c|)^2$, where the weight w is $\sigma(|F_o|)^{-2}$, the reciprocal square of the standard deviation of each observation, $|F_o|$. Neutral atom scattering factors for Fe, P, O, C,[8] and H[9] were used in the calculations, and the real ($\Delta f'$) and imaginary ($\Delta f''$) corrections[8] for anomalous X-ray scattering were applied to the Fe and P scattering curves.

Full-matrix least-squares refinement, using the 4890 reflections with $I_o/\sigma(I_o) > 2$, converged for a model in which phenyl groups were treated as rigid groups,[10] nongroup nonhydrogen atoms as anisotropic thermal ellipsoids, and nongroup hydrogen atoms as isotropic atoms, with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.049$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.053$, and a standard deviation of an observation of unit weight $= [\sum w(||F_o| - |F_c||)^2/(m - s)]^{1/2} = 2.78$ for $m = 4890$ observations and $s = 180$ variables. Inspection of the data indicated no evidence of secondary extinction. A structure factor calculation with all 5802 reflections measured during data collection gave R and R_w indices of 0.059 and 0.053, respectively.

In the final cycle of refinement, the largest shifts in nongroup nonhydrogen and nongroup hydrogen parameters were, respectively, less than 4 and 15% of a corresponding estimated standard deviation (esd), while the largest shifts in the group parameters were less than 44% of an appropriate esd. There were several peaks with heights of 0.4–0.8 e Å^{-3} on a final difference Fourier map which either were ca. 1 Å from the Fe or P atoms or were due to anisotropy of the rigid group atoms.

Table I. Crystallographic Summary for $(C_4H_4)Fe(P(C_6H_5)_2CH_2-)_2(CO)$

Crystal Data at −35 °C[a]

empirical formula	$C_{31}H_{28}FeOP_2$	d_{measd}, g cm^{-3} (19 °C; flotation in aq $ZnCl_2$)	1.45
fw	534.39		
a, Å	9.608 (8)	d_{calcd}, g cm^{-3} (−35 °C)	1.414 (4)
b, Å	14.694 (3)		
c, Å	9.473 (2)	cryst system	triclinic
α, deg	103.30 (1)	space group	$P1$ (No. 1) or $P\bar{1}$ (No. 2)[b]
β, deg	102.54 (2)		
γ, deg	92.73 (2)	Z	2
V, Å^3	1264 (4)	$F(000)$, e	556

Data Collection at −35 °C[c]

radiation (Mo Kα), Å	0.710 69
mode	ω scan
scan range	symmetrically over 1.0° about $K\alpha_{1,2}$ max
bkgd	offset 1.0 and −1.0° in ω from $K\alpha_{1,2}$ max
scan rate, deg min^{-1}	variable 2.0–5.0
check reflctns	4 remeasured after every 96 reflections; analysis of these data indicated a gradual decline in intensity of 2% during the 100 h of data collection for which the appropriate corrections were applied[d]
2θ range, deg	4.0–55.0
total reflctns measd	5802
data cryst dimens, mm	0.15 × 0.24 × 0.47
data cryst vol, mm^3	0.040
data cryst faces	$(01\bar{1})$, (100), $(\bar{1}00)$, (010), $(0\bar{1}0)$, $(00\bar{1})$, $(0\bar{1}1)$, $(11\bar{1})$, $(\bar{1}\bar{1}1)$
abs coeff, μ(Mo Kα), cm^{-1}	7.62
transmission factor range	0.74–0.88

[a] Unit cell constants were obtained by least-squares refinement of the setting angles of 60 reflections with $22.0 < 2\theta < 28.0°$. [b] Shown by successful refinement to be $P\bar{1}$ (see text). [c] Syntex $P2_1$ autodiffractometer equipped with a graphite monochromator and a Syntex LT-1 inert-gas low-temperature delivery system. [d] Henslee, W. H.; Davis, R. E. *Acta Crystallogr., Sect B* **1975**, *31*, 1511.

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

(7) A listing of the principal computer programs used in this study is provided in ref 6.

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

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

(10) The phenyl rings were constrained as follows: C–C = 1.392 Å, C–H = 1.00 Å, C–C–C = 120°. Each phenyl hydrogen atom was assigned an isotropic thermal parameter 1.0 Å^2 greater than that of the refined value of the carbon atom to which it is bonded.

Table II

a. Fractional Coordinates and Anisotropic Thermal Parameters (×10^4) for Nongroup Nonhydrogen Atoms[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe[b]	−0.17595 (4)	0.21381 (3)	0.23931 (4)	2848 (22)	2524 (21)	2414 (20)	448 (16)	798 (16)	812 (16)
P(1)[b]	0.03870 (8)	0.19635 (5)	0.20266 (8)	2934 (37)	2372 (34)	2289 (34)	697 (28)	606 (28)	608 (27)
P(2)[b]	−0.21187 (7)	0.27396 (5)	0.04663 (8)	2510 (36)	2567 (35)	2471 (35)	436 (27)	645 (28)	829 (28)
O	−0.2884 (3)	0.0198 (2)	0.0967 (3)	900 (21)	344 (13)	554 (16)	−153 (13)	112 (14)	76 (12)
C(1)	−0.3072 (4)	0.2939 (3)	0.3459 (4)	437 (19)	538 (21)	398 (18)	217 (16)	225 (15)	152 (16)
C(2)	−0.2795 (4)	0.2132 (3)	0.4057 (4)	443 (19)	518 (21)	359 (17)	47 (15)	210 (15)	133 (15)
C(3)	−0.1314 (4)	0.2496 (2)	0.4664 (3)	451 (19)	397 (17)	251 (15)	55 (14)	116 (14)	77 (13)
C(4)	−0.1595 (4)	0.3309 (2)	0.4057 (3)	503 (19)	328 (16)	301 (15)	92 (15)	153 (14)	40 (13)
C(5)	0.0140 (3)	0.1674 (2)	−0.0016 (3)	331 (16)	321 (15)	239 (14)	90 (13)	88 (12)	32 (12)
C(6)	−0.0722 (3)	0.2418 (2)	−0.0612 (3)	310 (15)	336 (15)	236 (14)	72 (13)	82 (12)	95 (12)
C(7)	−0.2423 (3)	0.0977 (2)	0.1506 (3)	451 (18)	341 (16)	339 (16)	9 (14)	86 (14)	128 (13)

b. Fractional Coordinates and Isotropic Thermal Parameters for Nongroup Hydrogen Atoms[a]

atom[c]	x	y	z	U, Å^2	atom[c]	x	y	z	U, Å^2
H(1)	−0.392 (4)	0.316 (2)	0.303 (4)	0.054 (11)	H(5,1)	0.100 (4)	0.161 (2)	−0.032 (4)	0.041 (9)
H(2)	−0.339 (4)	0.157 (3)	0.413 (4)	0.072 (12)	H(5,2)	−0.035 (4)	0.106 (2)	−0.039 (4)	0.045 (10)
H(3)	−0.053 (3)	0.232 (2)	0.533 (4)	0.038 (9)	H(6,1)	−0.116 (3)	0.219 (2)	−0.166 (4)	0.035 (8)
H(4)	−0.104 (3)	0.388 (2)	0.419 (3)	0.036 (8)	H(6,2)	−0.012 (3)	0.295 (2)	−0.050 (3)	0.027 (8)

c. Group Parameters for Rigid Phenyl Rings

group[d]	x_0	y_0	z_0	ϕ	θ	ρ
Ph(1)	0.1753 (2)	0.3002 (1)	0.2673 (2)	2.529 (1)	2.954 (1)	1.425 (1)
Ph(2)	0.1464 (2)	0.1050 (1)	0.2623 (2)	0.585 (1)	2.959 (1)	−0.615 (1)
Ph(3)	−0.1979 (2)	0.4042 (1)	0.0949 (2)	−2.652 (1)	2.823 (1)	3.023 (1)
Ph(4)	−0.3791 (2)	0.2463 (1)	−0.1021 (2)	1.540 (1)	−2.543 (1)	−2.287 (1)

[a] See Figure 1 for identity of the atoms. Numbers in parentheses throughout the table are estimated standard deviations in the units of the least significant digits for the corresponding parameter. The U_{ij} are the mean-square amplitudes of vibration in Å^2 from the general temperature factor expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] For Fe and P atoms the anisotropic thermal parameters are given ×10^5. [c] The sequence number of a hydrogen atom corresponds to that of the carbon atom to which it is bound. [d] See Figure 1 for identity of the group. For a description of these group parameters see: Eisenberg, R.; Ibers, J. A. *Inorg. Chem.* 1965, *4*, 773. Angular coordinates are in radians. The internal coordinate system of a phenyl ring has been defined elsewhere: Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B* 1975, *31*, 2928.

Atomic positional and thermal parameters and rigid-group parameters, with corresponding esd's as estimated from the least-squares inverse matrix, are given in Table II. Fractional crystallographic coordinates and isotropic thermal parameters, with esd's, for group atoms and a tabulation of observed and calculated structure factor amplitudes are available.[11]

Discussion of the Structure of $(C_4H_4)Fe(dppe)(CO)$

The crystal structure consists of discrete molecules of $(C_4H_4)Fe(dppe)(CO)$ with no unusual intermolecular contacts. Figure 1 provides a stereoscopic view of the molecule and indicates the atom numbering scheme used herein. Table III affords a listing of bond lengths and bond angles. The coordination geometry about Fe is approximately tetrahedral if the centroid of the cyclobutadiene ring is regarded as one vertex of a tetrahedron; the resulting (six) "tetrahedral" angles about Fe range from 86 to 127°. Bonding between Fe and the cyclobutadiene (cb) ring is symmetrical (Fe–C(cb) = 2.023 (3)–2.040 (4) Å, mean Fe–C(cb) = 2.033 (7) Å,[12] with the C_4 ring and the ML_3 fragment adopting an eclipsed conformation as discussed below. The C–C bonds of the cb ring average 1.443 (7) Å, with no bond length differing significantly from this value and with no internal cb ring angle deviating by more than 0.6° from 90°; hence the cb ring is virtually square and planar. Although the esd's are large, the cb hydrogen atoms appear to lie out of the plane of the C_4 ring in the direction away from the metal atom, an effect which is opposite to that generally observed for the hydrogen atoms of coordinated cyclopentadienyl rings.[13]

Comparison of the CO stretching frequency and Fe–C(carbonyl) and C–O bond lengths of $(C_4H_4)Fe(dppe)(CO)$ with the corresponding quantities of the monosubstituted phosphine complex $(C_8H_6)Fe(P(C_6H_5)_3)(CO)_2$[14] and the unsubstituted tricarbonyl complex $[(CO)_3Fe(C_4H_5)(CHOH)(C_2H_4)-]_2$[15] demonstrates the anticipated effects of systematic phosphine substitution upon residual metal–carbonyl bonding. These data are summarized in Table IV. The observed changes are generally attributed to an increase in Fe–CO back-bonding as a consequence of phosphine substitution. The structural correlations observed in a systematic study of a series of iron–phosphine–carbonyl complexes will be discussed in a forthcoming paper.[16]

As shown by the mean plane (see Table V) calculated with the positions of the Fe, P(2), C(5) and C(6) atoms, the C–P–Fe–P–C chelate ring exhibits an envelope conformation in which P(1) may be regarded as the "flap atom" of the envelope. The torsion angles about this ring are given in Table VI and may be compared to the values obtained for other metal–diphosphine ligand five-membered rings which have been compiled elsewhere.[17,18]

Figure 2 illustrates the packing of the $(C_4H_4)Fe(dppe)(CO)$ molecules in the crystal. Each molecule is surrounded by three

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(11) Supplementary material.

(12) A mean bond length, $\bar{l}$, for n bond lengths is given by $\bar{l} = \sum l_i/n$, and its standard deviation, $\sigma(\bar{l})$, by $\sigma(\bar{l}) = [\sum(l_i - \bar{l})^2/(n-1)]^{1/2}$.

(13) Displacement of the hydrogen atoms of coordinated cyclopentadienyl rings toward the metal has been clearly demonstrated by a recent neutron diffraction study of ferrocene: Takasagawa, F.; Koetzle, T. F. *Acta Crystallogr., Sect. B* **1979**, *35*, 1074.

(14) Davis, R. E., unpublished results.

(15) The crystal structure has been reported: Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B* **1978**, *34*, 3760.

(16) Riley, P. E.; Davis, R. E., manuscript in preparation.

(17) Riley, P. E.; Capshew, C. E.; Pettit, R.; Davis, R. E. *Inorg. Chem.* **1978**, *17*, 408.

(18) Hall, M. C.; Kilbourn, B. T.; Taylor, K. A. *J. Chem. Soc., A* **1970**, 2539.

(19) It should be noted that, although the molecular structure of (π-C_4H_4)$Fe(CO)_3$ has been established by gas-phase electron diffraction, the stereochemistry of the $Fe(CO)_3$ fragment vis-à-vis the C_4 ring could not be determined; see ref 2.

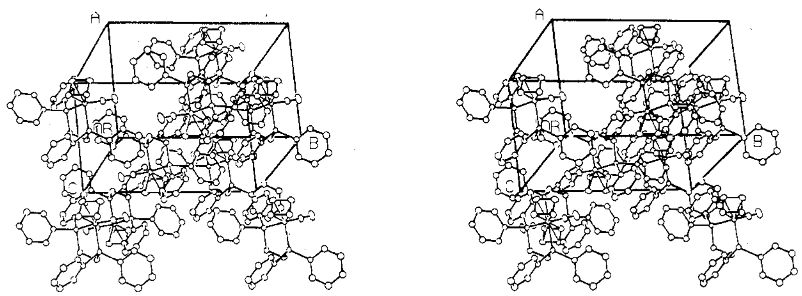

Figure 2. Stereoscopic view of the environment of a $(C_4H_4)Fe(dppe)(CO)$ molecule. Atoms are drawn as ellipsoids of 30% probability; hydrogen atoms have been omitted for sake of clarity.

Table III. Bond Lengths (Å) and Bond Angles (Deg) for Nongroup Atoms[a]

	Bond Lengths		
Fe-P(1)	2.181 (1)	C(2)-C(3)	1.441 (5)
Fe-P(2)	2.175 (1)	C(3)-C(4)	1.453 (5)
Fe-C(1)	2.033 (4)	C(1)-C(4)	1.440 (5)
Fe-C(2)	2.040 (4)	C(5)-C(6)	1.537 (4)
Fe-C(3)	2.036 (3)	C(7)-O	1.165 (4)
Fe-C(4)	2.023 (3)	C(1)-H(1)	0.94 (4)
Fe-C(7)	1.742 (3)	C(2)-H(2)	1.01 (4)
P(1)-C(5)	1.843 (3)	C(3)-H(3)	0.96 (3)
P(1)-C(11)*	1.863 (2)	C(4)-H(4)	0.94 (3)
P(1)-C(21)*	1.848 (2)	C(5)-H(5,1)	0.94 (3)
P(2)-C(6)	1.870 (3)	C(5)-H(5,2)	0.95 (4)
P(2)-C(31)*	1.854 (2)	C(6)-H(6,1)	0.96 (3)
P(2)-C(41)*	1.852 (2)	C(6)-H(6,2)	0.92 (3)
C(1)-C(2)	1.438 (5)		
	Bond Angles		
P(1)-Fe-P(2)	85.6 (1)	Fe-P(2)-C(6)	110.0 (1)
P(1)-Fe-C(7)	94.4 (1)	Fe-P(2)-C(31)*	113.9 (1)
P(1)-Fe-cb[b]	126.6 (1)	Fe-P(2)-C(41)*	123.1 (1)
P(2)-Fe-cb[b]	120.9 (1)	C(6)-P(2)-C(31)*	105.2 (1)
P(2)-Fe-C(7)	99.4 (1)	C(6)-P(2)-C(41)*	102.2 (1)
C(7)-Fe-cb[b]	121.4 (1)	C(31)*-P(2)-C(41)*	100.7 (1)
Fe-P(1)-C(5)	104.8 (1)	C(4)-C(1)-C(2)	90.1 (3)
Fe-P(1)-C(11)*	118.9 (1)	C(1)-C(2)-C(3)	90.5 (3)
Fe-P(1)-C(21)*	122.6 (1)	C(2)-C(3)-C(4)	89.4 (3)
C(5)-P(1)-C(11)*	103.2 (1)	C(3)-C(4)-C(1)	90.0 (3)
C(5)-P(1)-C(21)*	104.3 (1)	Fe-C(7)-O	177.1 (3)
C(11)*-P(1)-C(21)*	100.8 (1)		

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits. See Figure 1 for identity of the atoms. Atoms marked with asterisks are rigid-group atoms. Angles involving hydrogen atoms vary as follows: P-C-H, 107 (2)-113 (2)°; C-C-H (of dppe), 110 (2)-112 (2)°; H-C-H (of dppe), 104 (3) and 108 (3)°; C-C-H (of C_4H_4), 132 (2)-137 (2)°.

Table IV. Structural Parameters for Some Iron-Carbonyl Complexes

	$[(CO)_3Fe(C_4H_5)$-$(CHOH)(C_2H_4)$-$]_2$[b]	$(C_8H_6)Fe(P$-$(C_6H_5)_3)(CO)_2$[c]	$(C_4H_4)Fe$-(dppe)(CO)[d]
Fe-C(CO), Å[a]	1.788 (7)	1.758 (18)	1.742 (3)
C-O, Å[a]	1.139 (3)	1.151 (4)	1.165 (4)
ν(CO), cm^{-1}	1975, 1990, 2030 (diethyl ether)	1920, 1970 (cyclohexane)	1880 (cyclohexane)

[a] The mean bond lengths are given for the first two complexes. Numbers in parentheses are the estimated standard deviations in the least significant digits. [b] Reference 15. [c] Reference 14. [d] This work.

other molecules at ~3.5 Å and by five more molecules at ~3.75 Å. No simple type of molecular packing is apparent.

Assessment of Stereochemical Distortions in Cyclobutadiene-ML_3 Complexes

For an idealized cyclobutadiene-ML_3 complex, i.e., one in which a fourfold axis of the ring coincides with a threefold axis of the ML_3 fragment, there may exist the two symmetrical structures **1** (eclipsed) and **2** (staggered), which are interconvertible by rotation of ML_3 by 15° (see drawings in Introduction). In order to examine trends in stereochemical features of the $(C_4R_4)ML_3$ complexes listed in Table VII and shown in Figure 3, we have arbitrarily chosen to describe the deviations from idealized geometry in terms of three factors—offset of ML_3 from the central position "below" the ring, tilt of the ML_3 fragment with respect to the ring, and torsion of ML_3 relative to the idealized structures **1** and **2**. The analyses were carried out by the following scheme, which is designed to lessen the effects of individual distortions from three- and fourfold symmetry and from individual deviations among bond lengths.

(1) The centroid of the ring was calculated as the unweighted arithmetic mean position of the ring carbon atoms. The distance between the projection of M onto the ring and the ring centroid position is termed the *offset* of ML_3.

Table V. Selected Mean Planes[a]

atom	dev from planes,[b] Å	atom	dev from planes,[b] Å
$0.4483X - 0.2788Y - 0.8493Z + 5.3441 = 0$			
C(1)*	−0.001 (4)	H(1)	−0.13 (4)
C(2)*	0.001 (3)	H(2)	−0.06 (4)
C(3)*	−0.001 (3)	H(3)	−0.11 (3)
C(4)*	0.001 (3)	H(4)	−0.12 (3)
		Fe	1.7581 (4)
$-0.5142X - 0.6533Y - 0.5557Z + 1.6603 = 0$			
Fe*	−0.0323 (4)	C(6)*	−0.072 (3)
P(2)*	0.0581 (7)	P(1)	−0.8419 (7)
C(5)*	0.046 (3)		

[a] Orthonormal (Å) coordinate system with axes *X*, *Y*, and *Z* parallel to unit cell vectors *a*, *c** × *a*, and *c**. A negative deviation from the plane indicates that the atom with coordinates given in Table II lies between the plane and the origin of the unit cell. See Figure 1 for identity of the atoms. [b] Numbers in parentheses are the estimated standard deviations in the least significant digits.

Table VI. Torsion Angles about the Bonds of the C-P-Fe-P-C Ring

bond[a]	torsion angle, deg	bond[a]	torsion angle, deg
Fe-P(2)	17.0	C(5)-P(1)	−51.4
P(2)-C(6)	10.1	P(1)-Fe	35.6
C(6)-C(5)	38.0		

[a] See Figure 1 for identity of the atoms.

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(20) Dunitz, J. D.; Mez, H. C.; Mills, O. S.; Shearer, H. M. M. *Helv. Chim. Acta* **1962**, *45*, 647.
(21) Crump, D. B.; Payne, N. C. *Inorg. Chem.* **1973**, *12*, 1663.
(22) Dodge, R. P.; Schomaker, V. *Acta Crystallogr.* **1965**, *18*, 614.
(23) Davis, R. E.; Simpson, H. D.; Grice, N.; Pettit, R. *J. Am. Chem. Soc.* **1971**, *93*, 6688. Simpson, H. D.; Davis, R. E., unpublished results.
(24) Oliver, J. D. Ph.D. Dissertation, The University of Texas at Austin, 1971.

Table VII. Selected Geometrical Parameters Derived from X-ray Crystallographic Results for (π-C_4R_4)ML_3 Complexes

compd	compd designator	offset, Å	tilt, deg	MTA,[c] deg	ϕ, deg	ref
idealized symmetrical structure (eclipsed)	**1**	---	---	0, 30, 30	0	
$(C_4H_4)Co(Co(CO)_4)(CO)_2$	A	0.08	4.0	0, 23.8, 23.8	0	4
$[C_4H_2(CH_3)(C(O)CH_3)]Fe(CO)_3$	B	0.08	2.3	1.4, 29.7, 32.2	1.3	14
$[(C_4(CH_3)_4)NiCl_2]_2$	C	0.06	2.4	4, 34, 36	2.0	20
$[(C_4(CH_3)_4)Pt(P(C_6H_5)(CH_3)_2)_2(CF_3)]^+SbF_6^-$	D	0.29	12.5	2.2, 15.2, 23.5	3.5	21
$(C_4(C_6H_5)_4)Fe(CO)_3$	E	0.05	2.8	2, 26, 35	3.7	22
$(C_4H_4)Fe(P(C_6H_5)_2CH_2-)_2(CO)$	F	0.02	3.7	7.7, 36.5, 41.0	4.1	this work
$(C_8H_6)Fe(P(C_6H_5)_3)(CO)_2$[a]	G	0.20	9.7	1.6, 20.0, 40.1	7.2	14
	H	0.22	9.7	7.4, 18.2, 38.4	9.2	14
$(C_4H_3HgCl)Fe(CO)_3$	I	0.14	5.0	5.2, 13.9, 39.8	10.4	14
$\{[(C_4H_3)_2(C_6H_5)C](Fe(CO)_3)_2\}^+BF_4^-$[b]	J	0.08	1.1	12.7, 28.6, 48.9	11.0	23
	L	0.07	3.2	16.3, 21.4, 48.6	14.5	23
$[C_8H_5(C(O)OCH_3)]Fe(CO)_3$	K	0.13	5.0	9.4, 14.5, 41.8	12.2	24
idealized symmetrical structure (staggered)	**2**	---	---	15, 15, 45	15	

[a] Crystal structure contains two independent molecules per unit cell which are denoted here as compounds G and H. [b] Each cation possesses two complexed cyclobutadiene-$Fe(CO)_3$ moieties which are referred to as complexes J and L; see ref 23. [c] Three minimum torsion angles.

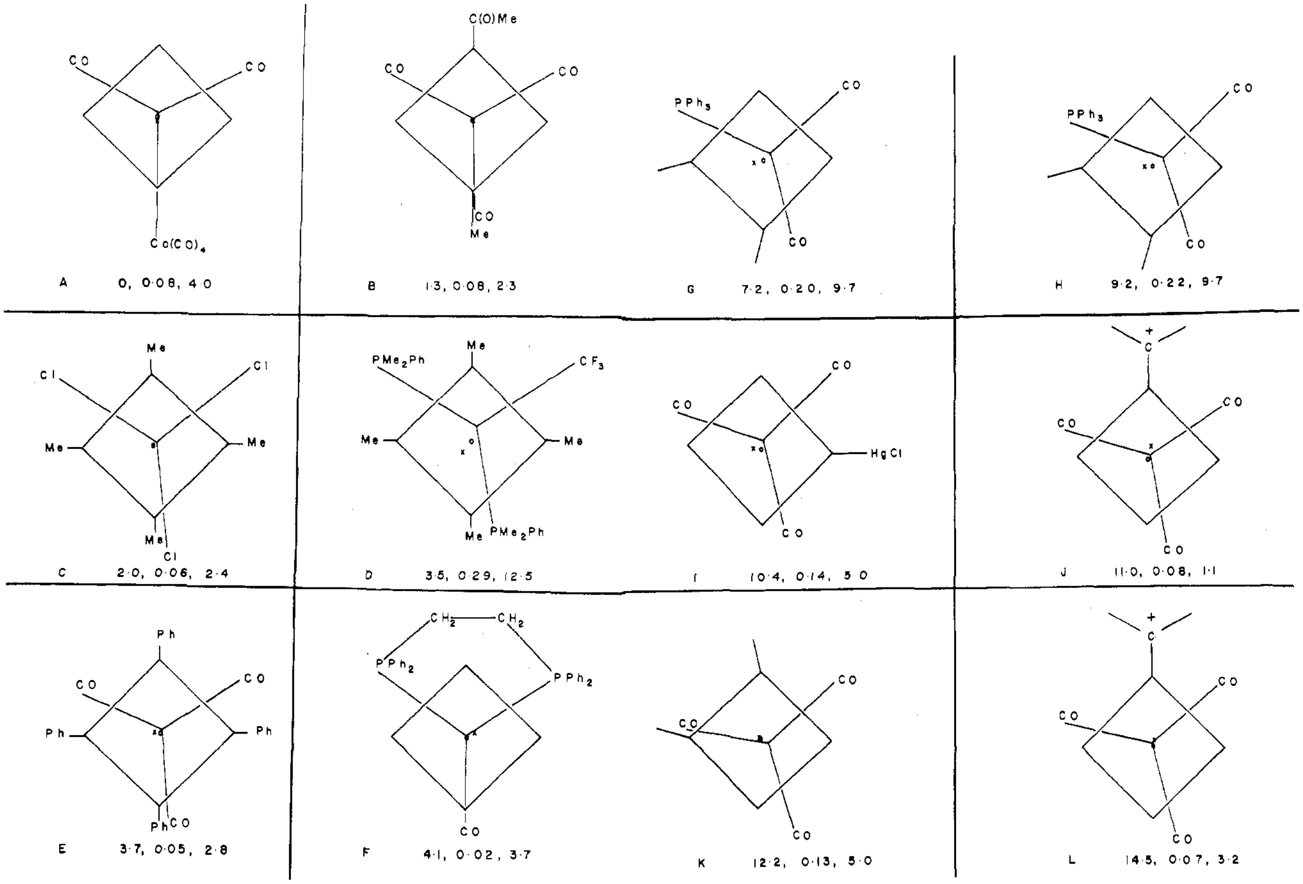

Figure 3. Projections of the (π-C_4R_4)ML_3 complexes onto the planes of the C_4 rings with the ML_3 fragments lying below the corresponding planes. Me and Ph denote methyl and phenyl substituents of the C_4 rings; positions of ring fusion in benzocyclobutadiene complexes G, H, and K are indicated. "O" and "X" represent the positions of the ring centroid and the point of intersection of the axis of the ML_3 cone with the cyclobutadiene mean plane, respectively. The compound designator (see Table VII) is given in the lower left-hand corner of each projection along with the values of ϕ (deg), offset (Å), and tilt (deg) (from left to right) for each complex (see Table VII). The compound designators are arranged in order of increasing ϕ.

(2) The directions of the three M–L bonds were taken to define a cone. The angle between the axis of this cone and the normal to the mean plane of the ring carbons is taken as the measure of the *tilt* of ML_3. The point at which this axis intersects the mean plane of the ring carbon atoms is denoted as X.

(3) Individual torsion angles of the form L_m–M–X–$C(cb)_n$ were computed for each complex, where L_m are the ligands of the ML_3 triad (m = 1–3) and $C(cb)_n$ are the cyclobutadiene ring carbon atoms (n = 1–4). For each complex, the smallest torsion angle for each of the three ligands L_m was selected. This set of three torsion angles, ordered by increasing magnitude, is termed the set of minimum torsion angles (MTA) for the complex. The torsion of the ML_3 group can be described by a *group torsion angle* ϕ (deg), in terms of the MTA. Let us represent the MTA for the idealized structures as Q_i and denote idealized structure **1** by $\phi = 0°$ (Q_i = 0, 30, 30°). As an idealized ML_3 is rotated through angle ϕ, the Q_i values are described by (1), so that **2** is described by $\phi = 15°$ (Q_i = 15, 15, 45°). Thus, for the idealized cyclobutadiene–ML_3

$$Q_1 = 0 + \phi \qquad Q_2 = 30 - \phi \qquad Q_3 = 30 + \phi \qquad (1)$$

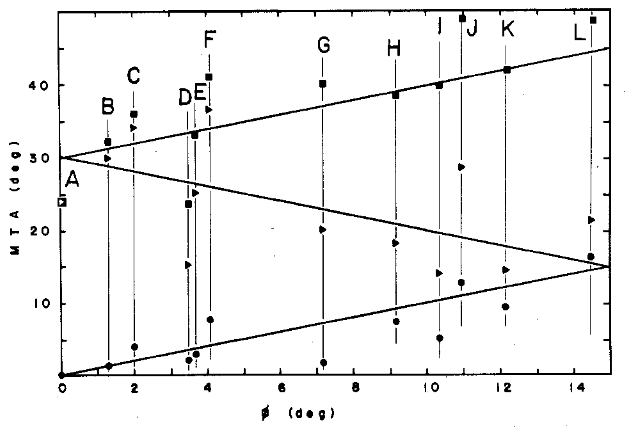

Figure 4. A plot of the observed MTA for each $(\pi\text{-}C_4R_4)ML_3$ complex as a function of its derived rotation angle ϕ. The three MTA are symbolized by ●, ■, and ▲ and are connected by thin vertical lines which are labeled in accordance with Table VII. The idealized MTA for **1** ($\phi = 0°$) and **2** ($\phi = 15°$) are joined by broad lines.

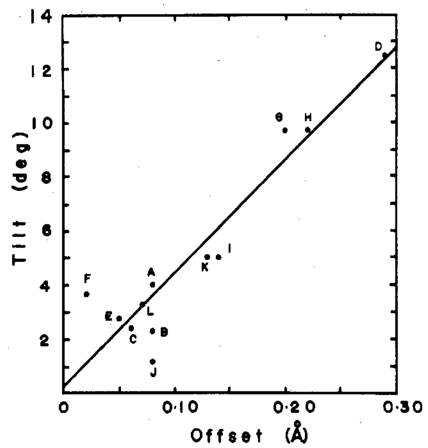

Figure 5. Plot of tilt (deg) vs. offset (Å). The points are labeled in accordance with Table VII. The equation of the least-squares line is tilt = 42(offset) + 0.2. The correlation coefficient for these data is 0.94; however, when the two points F and J (see text) are omitted, the correlation coefficient is 0.98.

complex, the MTA would follow the three solid lines of Figure 4. For the real structures to be characterized, we arrive at the value of ϕ by minimization with respect to ϕ of the expression $\sum_{i=1,3}(\text{MTA}_i - Q_i)^2$, in which the MTA_i are the three values observed for the complex and the Q_i are given by (1). The resultant expression for ϕ is given by (2).

$$\phi = (|\text{MTA}_1| - |\text{MTA}_2| + |\text{MTA}_3|)/3 \qquad (2)$$

Discussion of $(C_4R_4)ML_3$ Stereochemistry

It is noteworthy that the metal atom seldom resides on the axis of the cyclobutadiene ligand but, probably as a consequence of steric effects and bonding interactions, is shifted by 0.1–0.3 Å from it. Furthermore, it is interesting that in no $(\pi\text{-}C_4R_4)ML_3$ structure examined herein is the ML_3 cone normal to the C_4 ring; i.e., the tilt is not equal to 0°. While the smaller deviations from perpendicularity may be ascribed to *inter*molecular contacts, the larger distortions more likely result from *intra*molecular (i.e., steric) contacts.

As illustrated in Figure 5, the relationship between tilt and offset is, as might be expected, linear. The two greatest deviations from the least-squares line of Figure 5 occur with the bulky chelate diphosphine-containing complex F and with the C_4 ring of complex J of the carbonium species.

Figure 4 is a plot of the observed MTA for each complex as a function of its derived angle ϕ. The three MTA of each complex are symbolized by a circle, a triangle, and a square and are connected by thin vertical lines. The idealized MTA for **1** (0, 30, 30°; $\phi = 0°$) and **2** (15, 15, 45°; $\phi = 15°$) are joined by broad lines and illustrate the expected values of the MTA for idealized structures which are intermediate to **1** and **2**, i.e., those with $0 < \phi < 15°$. The points which emerge from this plot are the rather good agreement between the predicted and observed values for the MTA and the distribution of the torsion parameters over the entire range between those of the two idealized symmetrical structures (**1** and **2**), which support the experimental results and theoretical suggestions[5] of a low rotation barrier in these complexes.

In complexes exhibiting less satisfactory agreement, the deviations appear to be comprehensible. Thus, the three MTA for $[(C_4(CH_3)_4)NiCl_2]_2$, complex C (see Figure 4), have values which exceed the anticipated values for $\phi = 2.0°$; this is probably a consequence of its dimeric structure in which the bridging Cl atoms subtend an angle of only 88° at the Ni atom. In the Pt-containing complex D two of the three MTA are substantially less than the idealized values (for $\phi = 3.5°$). This may be understood in terms of its considerable offset (0.29 Å) and tilt (12.5°), both of which can be attributed to the bulk of the $P(CH_3)_2(C_6H_5)$ ligands. Similarly, the departure of the MTA of complex F from expectations is doubtlessly due to the bulk of the phosphine ligands and the strain of the chelate ring. Although complexes G and H are identical benzocyclobutadiene complexes which exist as two crystallographically independent molecules within the same unit cell, the MTA of G deviate somewhat from the expected values, while those of H fall much closer to the anticipated angles. We can offer no explanation for this.

The carbonium ion containing J and L has potential C_2 symmetry; thus the differences in stereochemical results for these two fragments (see Figures 4 and 5) are at first somewhat unsettling. In each fragment J and L, one Fe–CO bond lies, in projection, nearly perpendicular to a ring C–C bond—i.e., $\phi \approx 15°$. In J, this unique carbonyl ligand lies very near the phenyl ring. In L, on the other hand, all three Fe–CO bonds are well removed from close intramolecular contacts. We note that it is fragment J which shows the most marked deviation in both the tilt–offset comparison and the MTA vs. ϕ plot. Presumably, this distortion is attributable to interionic contacts in the crystal.

In solution (and in the gas phase for $(C_4H_4)Fe(CO)_3$[19]) the cyclobutadiene ring of each of these complexes has been shown to rotate freely with respect to its ML_3 fragment. As observed by Hoffmann et al.,[5] a coordinated cyclobutadiene ring possesses two perpendicular vertical mirror planes. Upon rotation the π orbitals of cyclobutadiene will encounter mutually orthogonal orbitals of the ML_3 fragment (essentially metal d orbitals) which are equally suited to overlap with the appropriate orbitals of the ring. Accordingly, the barrier to rotation in these complexes must be quite low. For instance in the representative molecule $(C_4H_4)Fe(CO)_3$, Hoffmann has calculated this barrier to be only 0.002 kcal mol^{-1}. Hence several nearly equivalent orientations of C_4 ring and ML_3 fragment are possible, and, since repulsive intra- or intermolecular contacts may be readily alleviated by rotation and/or ML_3 translation (offset), it is not suprising to find in the solid state not only structures which approach **1** or **2** but also those which are intermediate in rotation. Since the bonding between ring and ML_3 fragment involves virtually pure metal d orbitals which are not greatly influenced by the nature of the ligands L, it is reasonable that the observed torsion angles ϕ are apparently not correlated with electronic differences in the ligands of an ML_3 group.

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to Professor Rowland Pettit and Dr. William Slegeir for providing a sample of $(C_4H_4)Fe(dppe)(CO)$ and to several other members of the Pettit research group for supplying samples of some of the other cyclobutadiene complexes which have been examined in this laboratory.

Registry No. $(C_4H_4)Fe(dppe)(CO)$, 72318-19-5.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes and of fractional coordinates and isotropic thermal parameters (28 pages). Ordering information is given on any current masthead page.

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Structural Characterization of the (Methylcyclopentadienyl)- and Cyclopentadienylnickel Carbonyl Dimers, $[Ni(\eta^5\text{-}C_5H_4R)(\mu\text{-}CO)]_2$ (R = CH_3, H): Stereochemical Analysis of Planar and Nonplanar $Ni_2(CO)_2$ Cores Containing Metal–Metal Single Bonds

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X-ray diffraction studies of $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ and $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ show, in accordance with their different solid-state infrared spectra, that the methyl-substituted cyclopentadienylnickel dimer crystallizes with a planar $Ni_2(CO)_2$ framework, in contrast to the unsubstituted dimer which crystallizes with *two* independent molecules A and B containing differently bent $Ni_2(CO)_2$ cores. The crystallographically imposed C_{2h}-$2/m$ site symmetry on the $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ molecule requires that each of the two centrosymmetrically related methylcyclopentadienyl rings is bisected by the mirror plane coincident with the planar $Ni_2(CO)_2$ core. This unsymmetrical ring orientation produces nonequivalent Ni–CO bond lengths of 1.840 (3) and 1.889 (3) Å (mean 1.864 Å). Molecules A and B of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ each conform within experimental error to C_{2v}-$2mm$ symmetry; the symmetrically disposed C_5H_5 rings, which are tilted such as to be almost perpendicular to their bonding planar NiC_2 fragments of the bent $Ni_2(CO)_2$ core, give rise to equivalent Ni–CO distances of range 1.853 (5)–1.874 (5) Å (mean 1.863 Å). An examination reveals that a bending deformation of the $Ni_2(CO)_2$ core from a planar one in the methylcyclopentadienyl carbonyl molecule to the differently bent ones in the cyclopentadienyl carbonyl molecules A and B (which possess torsional angles of 146.0 and 139.2°, respectively, for the CNi_2–Ni_2C' fragment) generates essentially no change in the Ni–C bond lengths and only a small alteration in the Ni–Ni distance (from 2.390 (1) to 2.363 (1) and 2.351 (1) Å for molecules A and B, respectively). Hence, an angular deformation of the $Ni_2(CO)_2$ core in molecules A and B may be simply considered as a bending vibrational mode of the two bridging carbonyl ligands about the Ni–Ni axis. The two independent molecules of crystalline $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ are then regarded as individual frames in a motion picture of a dynamic butterfly-like inversion, which is presumed from energetic considerations to occur in solution. In order to lead to an equivalent C_{2v} molecular configuration, an inversion of the nonplanar $Ni_2(CO)_2$ core must be accompanied by a concomitant rotation (together with a slight tilting) of each cyclopentadienyl ring by 36° about its Ni–Cp(centroid) axis. In this case, the intermediate structure corresponds to that of crystalline $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ with a planar $Ni_2(CO)_2$ core and perpendicular rings which have been rotated by 18°. The solid-state existence of this intermediate configuration thereby provides direct evidence that such a butterfly interconversion is structurally allowed with bridge retention. Both $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ and $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ were characterized by solution and solid-state infrared, by ^1H and $^{13}C\{^1H\}$ NMR, and by mass spectral measurements under matching conditions. $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$: mol wt = 331.68, monoclinic, $C2/m$, a = 8.009 (2) Å, b = 8.794 (3) Å, c = 9.971 (3) Å, β = 113.87 (1)°, V = 642.2 (7) $Å^3$, ρ_o = 1.71 g/cm^3 (flotation), ρ_c = 1.715 g/cm^3 for Z = 2. For 1612 independent diffractometry-collected reflections with $I > 2\sigma(I)$, $R_1(F)$ = 5.0% and $R_2(F)$ = 5.7%. $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$: mol wt = 303.63, triclinic, $P\bar{1}$, a = 10.990 (2) Å, b = 13.704 (2) Å, c = 7.860 (2) Å, α = 99.12 (1)°, β = 101.54 (2)°, γ = 75.94 (1)°, V = 1117.4 (4) $Å^3$, ρ_o = 1.77 g/cm^3 (flotation), ρ_c = 1.805 g/cm^3 for Z = 4. For 3879 independent diffractometry-collected reflections with $I > 2\sigma(I)$, $R_1(F)$ = 4.5% and $R_2(F)$ = 5.2%.

Introduction

In the course of research dealing with a resolution of crystallographic twinning and/or crystal disorder problems in triangular organometallic compounds of cobalt and nickel,[1] the (methylcyclopentadienyl)nickel carbonyl dimer,[2] $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$, was isolated. Our stereochemical interest in this methyl-substituted cyclopentadienyl derivative was aroused by its unexpectedly exhibiting a markedly different color and transparency in the crystalline state from that of the classical parent dimer, $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$.

This latter compound was first prepared in 1958 by Fischer and Palm[3] who from magnetic susceptibility measurements established its diamagnetic character and from its infrared spectrum proposed a carbonyl-bridged structure with a Ni–Ni bond. They also reported[3] from dielectric constant measurements[4] in benzene solution at 25 °C a permanent dipole moment of $\mu = 0 \pm 0.38$ D. The first suggestion of a bent geometry similar to that of the electronically equivalent $Co_2(CO)_8$ was made by Tilney-Bassett and Mills[5] on the basis of the compound exhibiting two carbonyl stretching frequencies in the bridging carbonyl region. Unpublished infrared investigations by Miller and Fritz and independently by Palm (both quoted by Miller[6]) showed the compound to possess two carbonyl stretching bands both in the solid state and in solution but only one band in the vapor at 100 °C. It is noteworthy that Miller[6] in 1962 mentioned that the proposed bent structure for $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ was difficult to reconcile with the compound's zero dipole moment, and consequently he suggested the possibility that the "free" molecule indeed has a center of symmetry but is slightly distorted in solution thereby allowing the second carbonyl frequency to become

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[1] Byers, L. R.; Uchtman, V. A.; Dahl, L. F., to be submitted for publication.

[2] "Gmelins Handbuch der Anorganischen Chemie"; Springer-Verlag: Berlin, 1974; Vol. 17, Part 2, pp 344–9.

[3] Fischer, E. O.; Palm, C. *Chem. Ber.* **1958**, *91*, 1725–31.

[4] (a) Fischer, E. O.; Schreiner, S. *Chem. Ber.* **1959**, *92*, 938–48. (b) Weiss, E. *Z. Anorg. Allg. Chem.* **1956**, *287*, 223–35.

[5] Tilney-Bassett, J. F.; Mills, O. S. *J. Am. Chem. Soc.* **1959**, *81*, 4757–8.

[6] Miller, J. R. *Adv. Inorg. Chem. Radiochem.* **1962**, *4*, 133–95.

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