Acta Cryst. (1981). B37, 442–444

Dicarbonylnitrosyl[1—3-η-4-*exo*-(trimethylphosphino)-1-cyclobutenyl]iron Hexafluorophosphate

By J. A. Potenza, R. Johnson, D. Williams and B. H. Toby

Department of Chemistry, Rutgers University, New Brunswick, New Jersey 08903, *USA*

R. A. Lalancette

Department of Chemistry, Rutgers University, Newark, New Jersey 07102, *USA*

and A. Efraty

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel

(*Received* 3 *July* 1980; *accepted* 22 *September* 1980)

Abstract. $[\{P(CH_3)_3C_4H_4\}Fe(CO)_2NO]^+.PF_6^-$, monoclinic, $P2_1/n$, $a = 14{\cdot}117\ (5)$, $b = 13{\cdot}138\ (4)$, $c = 8{\cdot}850\ (4)$ Å, $\beta = 100{\cdot}72\ (3)°$, $Z = 4$, $D_o = 1{\cdot}694\ (2)$, $D_c = 1{\cdot}709$ Mg m^{-3}; $R_F = 0{\cdot}059$, $R_{wF} = 0{\cdot}056$ for 1257 reflections. The structure contains discrete $[\{P(CH_3)_3C_4H_4\}Fe(CO)_2NO]^+$ cations with Fe coordinated to two terminal CO ligands, one terminal NO ligand, and the π-allyl fragment of the cyclobutenyl ring. The three monodentate ligands and the center of the allyl fragment surround the Fe atom in a distorted tetrahedral arrangement. The NO group is bent slightly [Fe—N—O, 172·7 (8)°] while bond distances within the allyl fragment [1·372 (12), 1·385 (12) Å] are significantly shorter than corresponding distances in other metal complexes containing cyclobutenyl ligands.

Introduction. The present structural investigation was undertaken as part of a project designed to prepare and characterize cyclobutadiene–metal and related complexes (review article, Efraty, 1977). The title complex (1) is the product of nucleophilic addition of trimethylphosphine to the coordinated cyclobutadiene complex $[(\eta^4\text{-}C_4H_4)Fe(CO)_2NO]^+.PF_6^-$; its preparation has been described previously (Efraty, Sandhu, Bystrek & Denney, 1977). Crystallization of (1) from acetone at 295 K yielded two forms, multifaceted prisms (major component) and needles (minor component). The needle form proved to be disordered and will be described briefly below.

A red-orange prism of dimensions 0·2 × 0·24 × 0·30 mm, mounted on a glass capillary, was used. Weissenberg and precession photographs indicated a monoclinic lattice and showed systematic absences consistent with space group $P2_1/n$ ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$). Cell dimensions were determined at 298(1) K from a least-squares fit of the setting angles of 15 reflections centered on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). With $Z = 4$, the observed (flotation, $CHCl_3/CHBr_3$) and calculated densities agreed well.

Data were collected (θ–2θ scan, 3610 independent reflections, $4 < 2\theta < 55°$) at 298(1) K using graphite-monochromated Mo $K\alpha$ radiation and the Syntex $P2_1$ diffractometer. Three standard reflections, recorded at 47-reflection intervals, showed a random variation of ±3%. A total of 1257 reflections having $F_o^2 \geq 3\sigma(F_o^2)$ were considered observed, corrected for Lp effects as well as the variation in standard intensities, and used in the structure solution and refinement. Standard deviations were assigned as $\sigma(F^2) = (\mathrm{Lp})^{-1} [N_t + (0{\cdot}03N_n)^2]^{1/2}$, where N_t is the total count and N_n is the net count. Absorption corrections were not applied ($\mu = 1{\cdot}23$ mm^{-1} for Mo $K\alpha$ radiation).

The structure was solved by the heavy-atom method and refined using full-matrix least-squares techniques. Neutral-atom scattering factors and anomalous-dispersion corrections for Fe and P were obtained from *International Tables for X-ray Crystallography* (1974). Refinement was based on F with weights derived from standard deviations estimated from counting statistics. Following isotropic refinement of the C, N, and O atoms, and anisotropic refinement of the Fe and P atoms, the cyclobutenyl H atom coordinates were calculated assuming ideal geometry and a C—H bond distance of 0·95 Å (Churchill, 1973); these coordinates were confirmed by difference electron density calculations. To locate methyl group H atoms, the appropriate group was rotated at 5° intervals and electron densities at the three H positions were calculated. The orientation with the highest combined electron density was used; for each methyl group, this orientation corresponded very nearly to an ideal configuration in which the methyl H atoms are staggered with respect to adjoining C(methyl) atoms. H

0567-7408/81/020442-03$01.00 © 1981 International Union of Crystallography

atom temperature factors were set according to $B_H = B_{eq} + 1$, where B_{eq} is the equivalent isotropic temperature factor of the atom bonded to H. H parameters were not refined. Several cycles of anisotropic refinement of all non-hydrogen atoms led to convergence with $R_F = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}059$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0{\cdot}056$. The largest calculated structure factor, F_{002}, was substantially larger than the value observed, possibly because of secondary extinction. This reflection was excluded from the refinement, but included in the final structure factor calculation. For the final cycle, all parameter changes were less than 0·03σ, where σ is the e.s.d. obtained from the inverse matrix. A final difference Fourier map showed a general background of ±0·35 e Å^{-3} and revealed no significant features.

Table 1. *Fractional atomic coordinates and isotropic thermal parameters*

Estimated standard deviations are given in parentheses. Equivalent isotropic temperature factors B_{eq}(Å^2) for the non-hydrogen atoms have been calculated by $B_{eq} = \frac{4}{3}(B_{11}a^{*2}a^2 + B_{12}a^*b^*ab\cos\gamma + \ldots)$.

	x	y	z	B_{eq}/B
Fe	0·17903 (9)	0·56337 (10)	0·26224 (15)	4·0
P(1)	−0·0097 (2)	0·2196 (2)	0·2609 (3)	4·8
P(2)	0·3486 (2)	0·6399 (2)	0·7102 (3)	3·7
O(1)	0·2140 (6)	0·7459 (6)	0·1135 (9)	8·0
O(2)	0·2266 (6)	0·3906 (5)	0·0759 (9)	7·0
O(3)	−0·0315 (6)	0·5348 (7)	0·1879 (11)	9·2
N	0·2052 (6)	0·6726 (6)	0·1802 (9)	4·9
C(1)	0·2908 (7)	0·5208 (8)	0·4404 (9)	4·5
C(2)	0·2016 (8)	0·4973 (8)	0·4711 (12)	5·4
C(3)	0·1811 (7)	0·5988 (8)	0·4921 (11)	5·0
C(4)	0·2872 (6)	0·6282 (6)	0·5141 (10)	3·4
C(5)	0·4754 (7)	0·6237 (8)	0·7180 (11)	5·8
C(6)	0·3254 (7)	0·7645 (7)	0·7775 (11)	5·3
C(7)	0·3065 (7)	0·5487 (7)	0·8334 (9)	4·8
C(8)	0·2056 (8)	0·4558 (8)	0·1483 (10)	5·2
C(9)	0·0488 (9)	0·5422 (8)	0·2193 (14)	6·8
F(1)	0·0675 (5)	0·1397 (6)	0·3273 (10)	12·2
F(2)	0·0456 (6)	0·2598 (6)	0·1382 (9)	12·3
F(3)	−0·0909 (5)	0·2990 (5)	0·2008 (8)	9·0
F(4)	−0·0614 (6)	0·1386 (5)	0·1471 (8)	10·6
F(5)	−0·0687 (6)	0·1817 (6)	0·3835 (8)	11·0
F(6)	0·0373 (5)	0·3012 (5)	0·3789 (8)	10·9
H(C1)	0·336	0·486	0·393	5·5
H(C2)	0·167	0·436	0·476	6·3
H(C3)	0·123	0·636	0·493	6·0
H(C4)	0·300	0·682	0·450	4·4
H(C5-1)	0·497	0·671	0·650	6·8
H(C5-2)	0·509	0·636	0·820	6·8
H(C5-3)	0·488	0·556	0·689	6·8
H(C6-1)	0·258	0·773	0·771	6·3
H(C6-2)	0·358	0·772	0·881	6·3
H(C6-3)	0·349	0·814	0·715	6·3
H(C7-1)	0·317	0·482	0·799	5·8
H(C7-2)	0·341	0·558	0·936	5·8
H(C7-3)	0·240	0·559	0·831	5·8

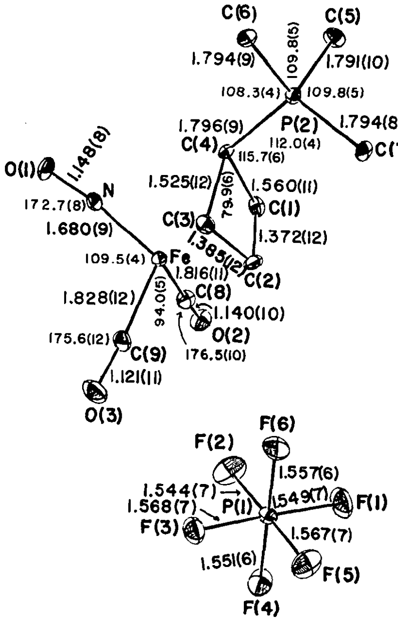

Fig. 1. *ORTEP* view (Johnson, 1965) of the title complex (8% probability ellipsoids) showing the atom-numbering scheme and bond distances (Å) and angles (°). Additional distances and angles are: Fe—C(1), 2·089 (9); Fe—C(2), 2·013 (10); Fe—C(3), 2·082 (10); Fe···C(4), 2·600 (8); Fe—CG, 1·842; N—Fe—C(8), 109·9 (4); C(8)—Fe—C(9), 94·0 (5); N—Fe—CG, 120·8; C(8)—Fe—CG, 110·0; C(9)—Fe—CG, 109·3; P(2)—C(4)—C(3), 115·5 (6); C(4)—P(2)—C(5), 109·1 (4); C(6)—P(2)—C(7), 107·8 (4); C(4)—C(1)—C(2), 91·1 (7); C(1)—C(2)—C(3), 91·9 (8); C(2)—C(3)—C(4), 92·1 (8).

Final atomic parameters are given in Table 1,* while a view of the structure, showing the atom-numbering scheme as well as selected bond distances and angles, is given in Fig. 1.

Discussion. The structure consists of discrete hexafluorophosphate anions and $[\{P(CH_3)_3C_4H_4\}Fe(CO)_2NO]^+$ cations with each Fe atom coordinated to two CO, one NO, and one $(CH_3)_3PC_4H_4$ ligand. If the cyclobutenyl group is assumed to occupy one coordination site, the Fe coordination geometry may be described as distorted tetrahedral with the largest contributions to angular distortion arising from the small C(8)—Fe—C(9) and large CG—Fe—N† angles [94·0 (5) and 120·8°, respectively]. The cation itself is substantially removed from point symmetry *m* as shown by deviations of the various atoms from the plane defined by Fe, C(2) and

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35684 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† CG is the center of gravity of the allyl fragment defined by atoms C(1), C(2), and C(3).

C(4). While P(2) lies only 0·01 Å from this plane and C(1) and C(3) are symmetrically removed (−1·00 and 0·98 Å, respectively), N, C(8) and C(9) show non-symmetric deviations (0·14, −1·41 and 1·25 Å) as do the methyl C atoms C(5)–C(7) (−1·56, 1·34 and 0·32 Å).

As indicated by the Fe—C(cyclobutenyl) distances, the cyclobutenyl group is bonded to Fe by the π-allylic fragment C(1)—C(2)—C(3) whose central atom C(2) lies approximately 0·07 Å closer to Fe than the terminal atoms, a pattern which has been observed previously for other metal–cyclobutenyl complexes [(2), $[\{(CH_3)_4C_4C_5H_5\}NiC_5H_5]$ (Oberhänsli & Dahl, 1965); (3), $[(CH_3)_3C_3COCo(CO)_3]$ (Potenza, Johnson, Mastropaolo & Efraty, 1974)]. Bond distances within the allyl fragment [1·372 (12), 1·385 (12) Å] are equivalent within experimental error and are significantly shorter than corresponding distances reported for (2) [1·439 (21), 1·444 (19) Å], (3) [1·450 (26), 1·480 (26) Å] and two derivatives of $[\{(C_6H_5)_4C_4OC_2H_5\}_2Pd_2Cl_2]$ [(4), 1·441 (22) – 1·477 (33) Å (Dahl & Oberhänsli, 1965)], all of which contain alkyl- or aryl-substituted cyclobutenyl ligands. The remaining structural features of the cyclobutenyl group, including the magnitude of the puckering of the C_4 ring [dihedral angle C(1)—C(2)—C(3)/C(3)—C(4)—C(1), 23·5°] and the relatively small angle at C(4) [79·9 (6)°] are comparable to those reported for (2) and (4).

Both the NO and CO groups are terminal, as indicated by the Fe—X—O (X = C, N) bond angles, while comparison of the Fe—N [1·680 (9) Å] and Fe—C [1·816 (11), 1·828 (12) Å] bond distances permits a clear distinction between the carbonyl and nitrosyl groups. The NO ligand is bent slightly [Fe—N—O, 172·7 (8)°] and to a greater degree than either CO group [Fe—C—O, 175·6 (12), 176·5 (10)°] or the terminal NO groups in $[Fe_4(NO)_4(\mu_3\text{-}S)_4]$ and $[Fe_4(NO)_4(\mu_3\text{-}S)_2\{\mu_3\text{-}NC(CH_3)_3\}_2]$[Fe—N—O, 176·9 (5)–179·4 (7)° (Gall, Chu & Dahl, 1974)]. Bonding parameters of the CO groups closely resemble those reported for other structures such as tricarbonyl-[5-*exo*-(triphenylphosphino)-1,3-cyclohexadiene]iron tetrafluoroborate (Guy, Reichert & Sheldrick, 1976).

The Me_3P-group P atom deviates 2·24 Å from the allyl plane and is *exo* to Fe. Atom P(2) shows nearly perfect tetrahedral coordination as indicated by the P—C bond distances [1·791 (10)–1·796 (9) Å] and C—P—C angles [107·8 (4)–112·0 (4)°] while in the PF_6 counterion, bond distances [1·544 (7)–1·568 (7) Å] and angles [87·1 (5)–95·0 (5)°] deviate only slightly from values expected for an octahedron.

The needle form of (1) yielded a trial structure similar to that of the monoclinic form. A needle, obtained from acetone, showed *mmm* reciprocal-lattice symmetry, lattice constants a = 13·933 (5), b = 9·904 (4), c = 11·947 (5) Å, Z = 4, and extinctions ($0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$) consistent with the orthorhombic space groups *Pnma* or $Pna2_1$. While attempts to solve the structure in $Pna2_1$ were unsuccessful, a trial structure consisting of all non-hydrogen atoms was obtained in *Pnma* and refined isotropically to $R_F = 0{\cdot}20$ using 581 reflections with $F^2 \geq 2\sigma(F^2)$. In *Pnma*, both the cation and anion occupy 4(c) sites of point symmetry m with the mirror plane of the cation containing Fe, C(2), C(4), P(2), one methyl C atom, and one monodentate XO ligand. Refinement was discontinued because of difficulties encountered in distinguishing the NO from the CO ligands. The needle-shaped crystals, which form almost exclusively during rapid crystallization from CH_2Cl_2/toluene, may represent a high-energy, disordered form of (1) containing mixed rotational isomers originating from a low barrier of rotation for the $Fe(CO)_2NO$ fragment about the Fe—CG axis.

We thank the Center for Computer and Information Services, Rutgers University, for providing computer time.

References

CHURCHILL, M. (1973). *Inorg. Chem.* **12**, 1213–1214.

DAHL, L. F. & OBERHÄNSLI, W. E. (1965). *Inorg. Chem.* **4**, 629–637.

EFRATY, A. (1977). *Chem. Rev.* **77**, 691–744.

EFRATY, A., SANDHU, S. S. JR, BYSTREK, R. & DENNEY, D. Z. (1977). *Inorg. Chem.* **16**, 2522–2526.

GALL, R. S., CHU, C. T.-W. & DAHL, L. F. (1974). *J. Am. Chem. Soc.* **96**, 4019–4023.

GUY, J. J., REICHERT, B. E. & SHELDRICK, G. M. (1976). *Acta Cryst.* B**32**, 2504–2506.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

OBERHÄNSLI, W. & DAHL, L. F. (1965). *Inorg. Chem.* **4**, 150–157.

POTENZA, J., JOHNSON, R., MASTROPAOLO, D. & EFRATY, A. (1974). *J. Organomet. Chem.* **64**, C13–C15.