

## Stability of the cyclobutenyl group in $\text{Fe}(\overline{\text{C}}=\text{CFCF}_2\overline{\text{CF}}_2)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ towards isomerisation by ring-opening. X-Ray crystal structures of $\text{Fe}(\overline{\text{C}}=\text{CFCF}_2\overline{\text{CF}}_2)(\text{CO})(\text{L})(\eta\text{-C}_5\text{H}_5)$ ( $\text{L} = \text{CO}$ and $\text{PPh}_3$ )

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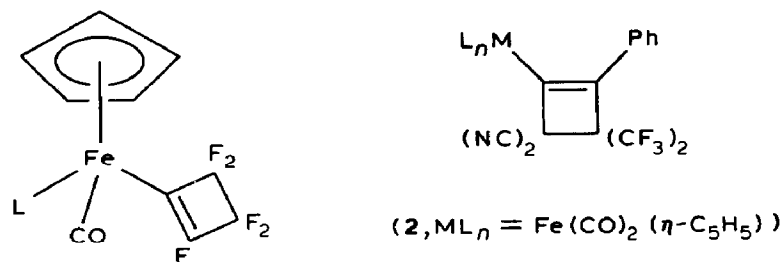
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### Abstract

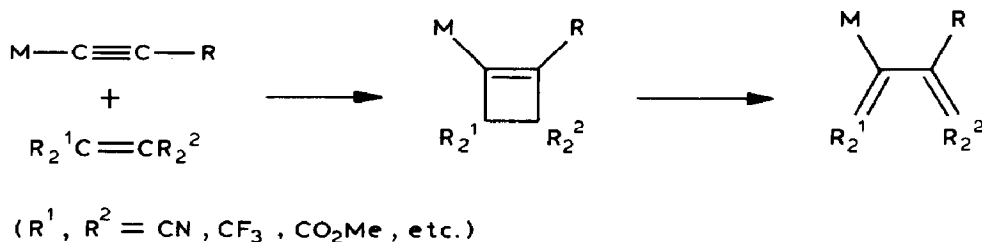
The perfluorocyclobutenyl-iron complex  $\text{Fe}(\text{c-C}_4\text{F}_5)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$  does not undergo ring-opening isomerisation to a buta-1,3-dien-2-yl derivative either on pyrolysis or on UV irradiation. This difference from related cyano-cyclobutenyl complexes, and from cyclobutenes in general, has been traced, by a structural study of the complexes  $\text{Fe}(\overline{\text{C}}=\text{CFCF}_2\overline{\text{CF}}_2)(\text{CO})(\text{L})(\eta\text{-C}_5\text{H}_5)$  ( $\text{L} = \text{CO}$  (**1a**),  $\text{PPh}_3$  (**1c**)), to a shorter (and therefore stronger) C–C bond opposite the C=C double bond, i.e. the bond that would be broken in the isomerisation reaction. Crystals of **1a** are monoclinic, space group  $P2_1/n$ , with unit cell dimensions  $a$  6.437(1),  $b$  15.864(4),  $c$  11.585(3) Å and  $\beta$  96.54(2)°, with  $Z = 4$ . Crystals of **1c** are triclinic, space group  $P\bar{1}$ , with cell parameters  $a$  9.358(8),  $b$  14.890(5),  $c$  17.865(4) Å,  $\alpha$  103.37(3),  $\beta$  95.06(4),  $\gamma$  91.13(5)°,  $Z = 4$ . Both structures were refined by full-matrix least-squares methods to final  $R$  of 0.041 and 0.072, for 766 and 2472 reflections with  $I > 2.5\sigma(I)$ , for **1a** and **1c**, respectively.

### Introduction

The synthesis of the complex  $\text{Fe}(\text{c-C}_4\text{F}_5)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$  (**1a**) was amongst the first experiments carried out by one of the present authors [1]. More recently, formal [2 + 2]-cycloaddition reactions of transition metal  $\sigma$ -acetylide complexes with certain electron-deficient olefins have been found to give related complexes containing cyclobutenyl rings, which undergo rather facile ring-opening reactions to form the isomeric buta-1,3-dien-2-yl derivatives (Scheme 1) [2–6]. The similarity of these complexes to **1a** prompted us to examine the tendency of the fluorinated compounds to participate in similar ring-opening reactions. These studies are reported herein, together with the molecular structures of the title complexes **1a** and **1c**.



- (1a, L = CO;  
 1b, L = NCMe;  
 1c, L = PPh<sub>3</sub>)



Scheme 1.

## Results and discussion

The perfluorocyclobutenyl complex **1a** is stable towards isomerisation promoted either by thermal or by photochemical means. The only reactions that we have been able to carry out successfully are simple CO-substitution by ligands such as acetonitrile or tertiary phosphines. Thus, irradiation of a solution of **1a** in acetonitrile gave the monocarbonyl **1b** in quantitative yield as an orange oil. This complex is quite sensitive towards oxidation, both in the pure state and in solution. Ready replacement of the acetonitrile by CO or tertiary phosphines, such as PPh<sub>3</sub>, afforded complexes **1a** or **1c** in 60 to 65% yields.

The new orange complexes **1b** and **1c** are readily soluble in hydrocarbon solvents. They were easily characterised by elemental microanalysis and from their spectroscopic properties. Whereas complex **1a** has two  $\nu(\text{CO})$  bands at 2052 and 2007  $\text{cm}^{-1}$ , the substituted complexes have only one, at 1966 (**1b**) or 1964  $\text{cm}^{-1}$  (**1c**). These bands show the expected lowering in frequency as a result of replacement of a CO ligand by a poorer  $\pi$ -acceptor ligand. In addition, the acetonitrile complex has a  $\nu(\text{CN})$  absorption at 2290  $\text{cm}^{-1}$ .

The <sup>1</sup>H NMR spectra contained resonances for the C<sub>5</sub>H<sub>5</sub> protons at  $\delta$  5.09 (**1a**), 4.68 (**1b**) and 4.58 ppm (**1c**), the latter as a doublet ( $J(\text{HP})$  1 Hz); the Me resonance of the coordinated MeCN ligand (**1b**) was found at  $\delta$  2.13 ppm. In the <sup>13</sup>C NMR spectra, the C<sub>5</sub>H<sub>5</sub> carbons resonated at  $\delta$  85.2 and 83.9 ppm for **1a** and **1c**, respectively, while the CO carbons are at  $\delta$  212.1 and 219.9 ppm. In **1a**, the four

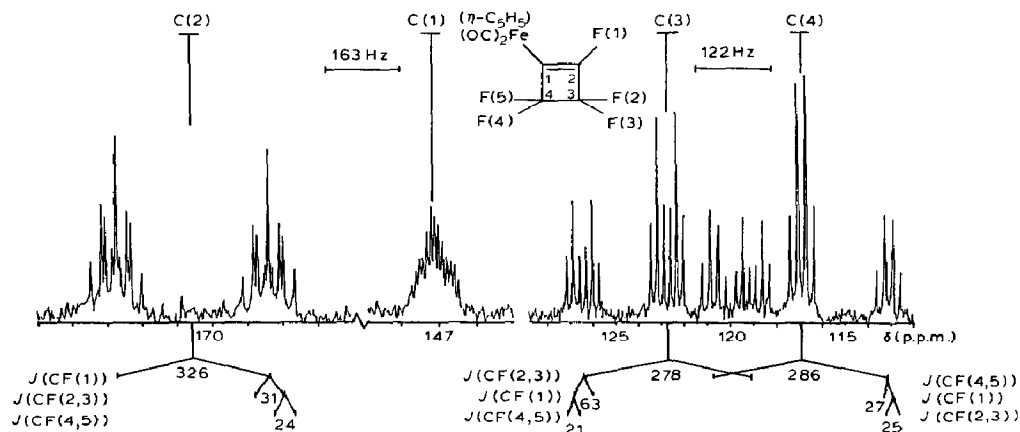


Fig. 1.  $^{13}\text{C}$  NMR spectrum of **1a**, cyclobutenyl ring carbon resonances, showing various  $J(\text{CF})$  couplings (Hz). Experimental conditions:  $\text{CH}_2\text{Cl}_2$  (1 M), 75.47 MHz, digital resolution 1.6 Hz/point.

cyclobutenyl ring carbons give the complex series of resonances shown in Fig. 1. From the fluorine couplings it has proved possible for the first time to make a positive assignment of these resonances. The doublet of multiplets centred on  $\delta$  170.8 ppm is assigned to C(2), each multiplet being two overlapping triplets of triplets. The complex multiplet at  $\delta$  147.2 ppm (13 peaks resolved) is assigned to C(1). Two further overlapping multiplets centred at  $\delta$  122.8 and 116.9 ppm are assigned to C(3) and C(4), respectively. The  $^{31}\text{P}$  NMR spectrum of **1c** contains a singlet at  $\delta$  75.2 ppm, no coupling to  $^{19}\text{F}$  being observed.

The  $^{19}\text{F}$  NMR spectra were obtained under conditions of higher resolution than was possible in 1965, slight changes in chemical shift values probably reflecting the increased accuracy and variations in temperature. For **1a** in  $\text{CS}_2$ , three signals at  $\delta$  -114.9, -114.1 and -110.0 ppm are assigned to F(4) and F(5), F(1), and F(2) and F(3), respectively, on the basis of their mutual coupling and relative intensities (see Experimental). A marked solvent effect is observed in  $\text{CH}_2\text{Cl}_2$ , with the two high field multiplets collapsing to a pseudo-triplet at  $\delta$  -116.0 ppm and the low field signal shifting to  $\delta$  -111.9 ppm. The  $\text{PPh}_3$  complex **1c** also exhibits a three-resonance pattern, but in this case two weakly interacting systems are present. In  $\text{CH}_2\text{Cl}_2$  solution F(4) and F(5) form an AB system centred on  $\delta$  -116.7 ppm, while F(1) ( $\delta$  -116.5) and F(2), F(3) ( $\delta$  -109.9) form an  $\text{A}_2\text{X}$  system. Pronounced solvent effects on these spectra were again observed. In  $\text{CS}_2$ , the AB signals overlap with the  $\text{A}_2\text{X}$  triplet at  $\delta$  -114.5 ppm, while in benzene, the AB and X multiplets coalesce to a broad triplet ( $\delta$  -115.8 ppm). The instability of **1b** precluded a detailed study of its  $^{19}\text{F}$  NMR spectrum.

The EI mass spectrum of **1a** has been described previously [7]. We have also obtained FAB mass spectra of **1b** and **1c**, which both contain molecular ions and strong  $[M - \text{CO}]^+$  ions as base peaks. Common fragmentation patterns include loss of F or  $\text{C}_5\text{H}_5$  and transfer of F or  $\text{CF}_2$  to the iron atom (by elimination of neutral  $\text{C}_4\text{F}_4$  or  $\text{C}_3\text{F}_3$  fragments, respectively). Thus in **1b**, major ions are  $[\text{FeCF}_2(\text{C}_5\text{H}_5)]^+$ ,  $[\text{FeF}(\text{C}_5\text{H}_5)]^+$  and  $[\text{Fe}(\text{C}_5\text{H}_5)]^+$ , while for **1c**, the  $\text{PPh}_3$  ligand is retained, giving  $[\text{FeCF}_2(\text{PPh}_3)]^+$ ,  $[\text{FeF}(\text{PPh}_3)]^+$  and  $[\text{Fe}(\text{PPh}_3)]^+$ .

We have determined the molecular structures of **1a** and **1c** by single-crystal X-ray

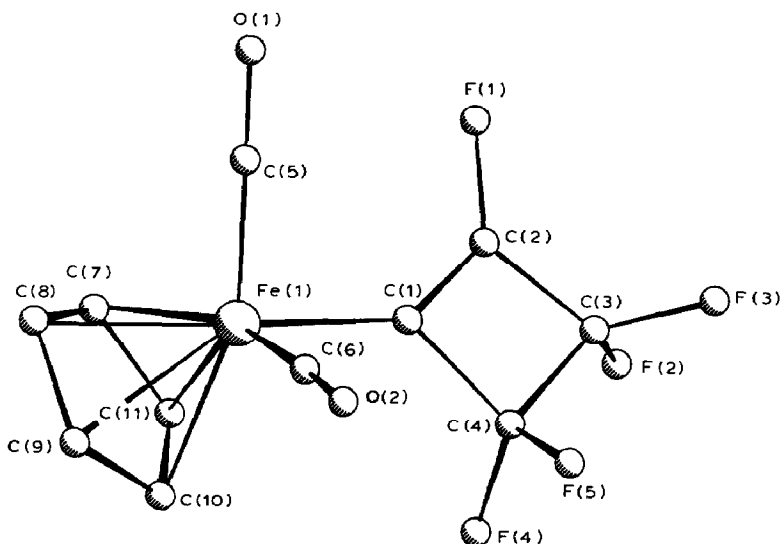


Fig. 2. Plot of molecular structure of  $\text{Fe}(\text{c-C}_4\text{H}_5)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$  (**1a**) showing atom numbering scheme.

diffraction methods to determine which structural factors result in the stability of these complexes compared with those derived from cyano-olefins. A plot of a molecule of **1a** is shown in Fig. 2, and Fig. 3 shows the two molecules, labelled **A** and **B**, comprising the asymmetric unit in **1c**. Selected bond parameters for these complexes are given in Table 1. In **1c**, the iron atoms are chiral centres, and the two molecules **A** and **B** have enantiomers generated by a centre of inversion in the centrosymmetric space group  $P\bar{1}$ , so that in all, there are four molecules of **1c** in the unit cell. Close examination of Fig. 3 shows that there are major differences between **A** and the enantiomer of **B**, although to a first approximation, **B** has the opposite chirality to **A**. The relative orientations of the fluorocarbon ring and the phosphorus-bound phenyl rings differ in **A** and **B**, as is clearly shown by the torsion angles  $\text{C}(10)\text{-Fe-C}(1)\text{-C}(2)$  ( $136.5^\circ$  for **A**,  $7.7^\circ$  for **B**). In **A**, the cyclobutenyl ring is oriented away from the  $\text{PPh}_3$  group, whereas in **B**, it occupies a void produced by rotation of the  $\text{PPh}_3$  group about the  $\text{Fe-P}$  bond. Alternatively, the  $\text{C}(4)=\text{C}(1)\text{-Fe-CO}(10)$  moieties are *transoid* in molecule **A**, and *cisoid* in molecule **B**.

The iron atom in **1a** has distorted octahedral geometry, with one octahedral face being occupied by the  $\text{C}_5\text{H}_5$  group [ $\text{Fe-C}(\text{cp})$  (av.)  $2.073(5)$  Å] and the other by the two CO groups [ $\text{Fe-C}(5)$   $1.74(1)$ ,  $\text{Fe-C}(6)$   $1.774(9)$  Å] and the cyclobutenyl carbon [ $\text{Fe-C}(1)$   $1.936(9)$  Å]. The angles subtended at iron by the three latter atoms [ $\text{C}(1)\text{-Fe-C}(5)$   $90.7(4)$ ,  $\text{C}(1)\text{-Fe-C}(6)$   $91.4(4)$ ,  $\text{C}(5)\text{-Fe-C}(6)$   $94.8(4)^\circ$ ] are all close to the expected octahedral angle. In the two molecules (**A** and **B**) of **1c**, the iron atoms have similar geometries. The cyclopentadienyl groups are slightly further away from the metal [ $\text{Fe-C}(\text{cp})$  (av.)  $2.093(8)$  Å for molecule **A**,  $2.111(7)$  Å for molecule **B**]. The other three sites are occupied by the CO [ $\text{Fe-C}(10)$   $1.72(2)$ ,  $1.73(2)$  Å],  $\text{PPh}_3$  [ $\text{Fe-P}$   $2.210(4)$ ,  $2.225(4)$  Å] and cyclobutenyl groups [ $\text{Fe-C}(1)$   $1.96(1)$ ,  $1.89(1)$  Å]. The angles subtended at iron by the donor atoms of these ligands [ $\text{C}(1)\text{-Fe-C}(10)$   $92.4(6)$ ,  $92.0(7)$ ;  $\text{C}(1)\text{-Fe-P}$   $96.4(5)$ ,  $92.2(4)$ ;  $\text{C}(10)\text{-Fe-P}$   $94.2(5)$ ,  $89.2(5)^\circ$ ] are also close to octahedral. The  $\text{Fe-C}(sp^2)$  bond lengths [ $1.936(9)$  Å in

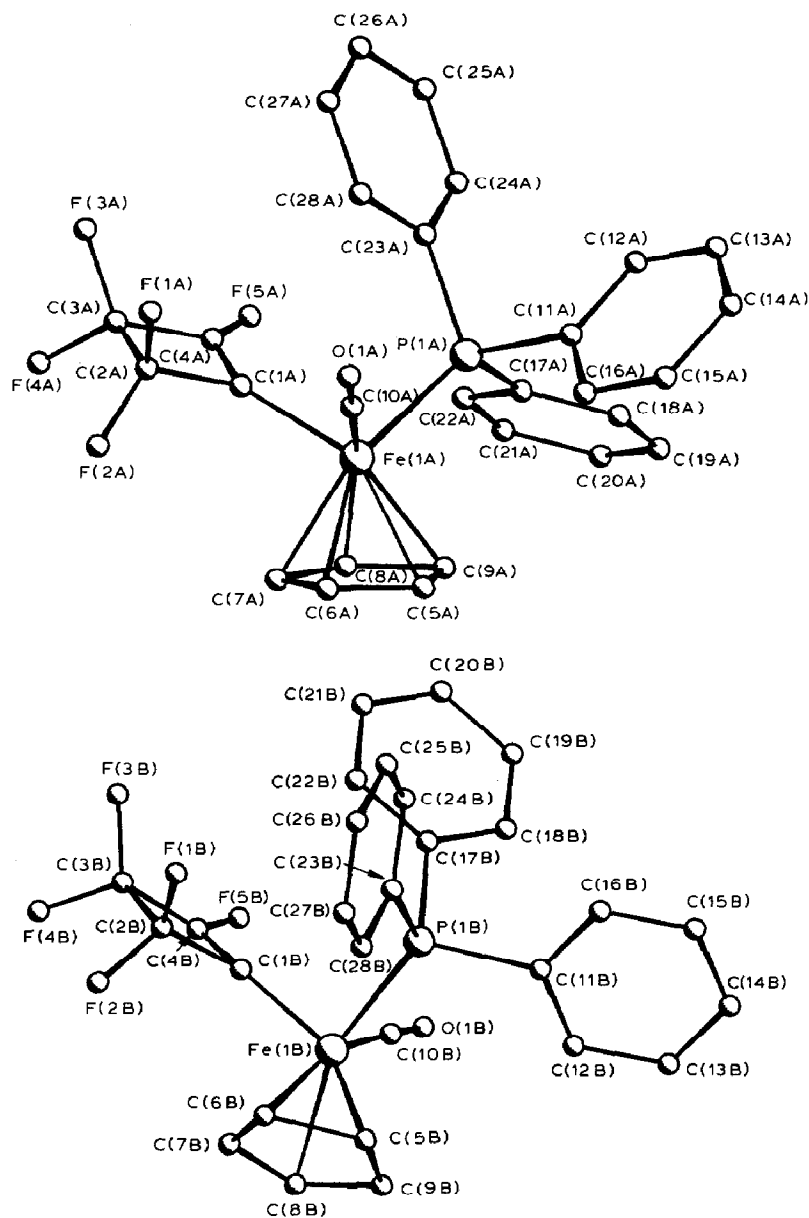
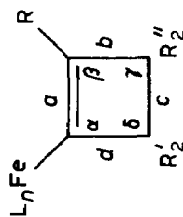


Fig. 3. Plot of molecular structures of the two independent molecules of  $\text{Fe}(\text{c-C}_4\text{F}_5)(\text{CO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$  (**1c**) showing atom numbering scheme.

**1a**, 1.93(1) Å (av.) in **1c** are similar to that found in **2** [1.949(4) Å] [5], but all are shorter than that found in the butadienyl complex  $\text{Fe}\{\text{C}=\text{C}(\text{CN})_2\}\text{CPh}=\text{C}(\text{CN})_2\text{-}(\text{CO})_2(\eta\text{-C}_3\text{H}_5)$  [1.972(2) Å] [4].

Of note in the context of the present investigation are the dimensions of the cyclobutenyl ring. Table 1 contains pertinent data for complexes **1a** and **1c**, together with those for complex **2** containing a  $\text{C}=\text{CPhC}(\text{CF}_3)_2\text{C}(\text{CN})_2$  ligand, formed by cycloaddition of  $(\text{CF}_3)_2\text{C}=\text{C}(\text{CN})_2$  to the corresponding phenylacetylide [5]. The tendency toward ring-opening in cyclobutenyl complexes so far studied is

Table 1  
Bond distances (Å) and angles (°) for the C<sub>4</sub> ring in some  $\sigma$ -cyclobutenyl iron complexes



FeL <sub>n</sub>	R	R'	R''	Fe-C	a	b	c	d	α	β	γ	δ	Reference
Fe(CO) <sub>2</sub> ( $\eta$ -C <sub>5</sub> H <sub>5</sub> )	F	F	F	1.936(9)	1.32(1)	1.48(1)	1.53(1)	1.51(1)	88.8(8)	99.4(8)	82.6(7)	89.1(7)	this work
Fe(CO)(PPh <sub>3</sub> )( $\eta$ -C <sub>5</sub> H <sub>5</sub> )	(A)	F	F	1.96(1)	1.35(2)	1.45(2)	1.54(2)	1.46(2)	89(1)	99(1)	82(1)	90(1)	this work
	(B)	F	F	1.89(1)	1.41(2)	1.42(2)	1.50(2)	1.49(2)	84(1)	100(1)	83(1)	93(1)	
Fe(CO) <sub>2</sub> ( $\eta$ -C <sub>5</sub> H <sub>5</sub> )	Ph	CN	CF <sub>3</sub>	1.949(4)	1.342(5)	1.534(5)	1.596(6)	1.577(5)	92.8(3)	96.6(3)	85.2(3)	85.4(3)	[5]

$\overline{\text{C}=\text{CPhC}(\text{CN})_2\text{C}(\text{CN})_2} > \overline{\text{C}=\text{CPhC}(\text{CF}_3)_2\text{C}(\text{CN})_2} \gg \overline{\text{C}=\text{CFCF}_2\text{CF}_2}$  and this observation can be related to the interatomic parameters, particularly the length, and thus the strength, of the bond opposite the C=C double bond in the cyclobutene ring, that is, the bond that is broken during the isomerisation process.

Irradiation of **1a** in non-coordinating solvents ( $\text{CH}_2\text{Cl}_2$ , petroleum spirit) using different UV sources (medium pressure 400 W, low pressure 16 W) produced gradual decomposition. Similarly pyrolysis of either **1a** or **1b** gave only decomposition under forcing conditions (120–140 °C). These observations are not entirely surprising, recent results having indicated that the activation energies for the thermal electrocyclic interconversion between perfluorosubstituted cyclobutenes and butadienes are around 37–40 kcal/mol [8]. In the same paper a marked increase in activation energy was noted if fluorine substituents were not able to rotate outwards in the course of the ring opening reaction. For **1a** therefore, both conrotatory (thermal) and disrotatory (photochemical) processes will be hindered. The related cyanocyclobutenyl complexes transform to the corresponding butadienes at room temperature. These results suggest that a paramount role is played by ring substituents in the cyclobutene–butadiene isomerisation reaction. Further papers will describe the stereochemistry of the isomerisation of related complexes, together with an assessment of the influence of several metal/ligand combinations on these reactions.

## Experimental

### *Experimental conditions*

All reactions were performed under  $\text{N}_2$  using dried, degassed solvents. Workup of **1b** was performed strictly under  $\text{N}_2$ ; otherwise, no special precautions were taken to exclude air during workup. Photochemical reactions were performed using Applied Photophysics 16 W low pressure and 400 W medium pressure mercury lamps in quartz immersion wells. Perfluorocyclobutene was purchased from Pfaltz and Bauer and was used as received.  $\{(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\}_2$  was purchased from Strem Chemicals.

### *Instrumentation*

IR: Perkin–Elmer 683 double-beam; NMR: Bruker CXP 300 spectrometer ( $^{19}\text{F}$  at 282.35 MHz,  $^{13}\text{C}$  at 75.47 MHz), Bruker WP 80 ( $^1\text{H}$  at 80 MHz). Chemical shifts to low field are denoted positive. Internal references were  $\text{CFCl}_3$  in  $\text{CS}_2$  or  $\text{C}_6\text{H}_6$  ( $^{19}\text{F}$ ) and TMS ( $^{13}\text{C}$  and  $^1\text{H}$ ); external references were  $\text{CFCl}_3$  in  $\text{CD}_2\text{Cl}_2$  ( $^{19}\text{F}$ ) and 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). For spectra obtained in non-deuterated solvents,  $\text{D}_2\text{O}$  or  $\text{CD}_2\text{Cl}_2$  in a concentric microtube was used for the field lock. Mass spectra: VG ZAB 2HF with FAB probe, Ar or Xe as the FAB gas, with source pressures typically  $10^{-6}$  mbar; FAB gun voltage 7.5 keV, current 1 mA, ion accelerating potential 8 keV. Spectra were obtained using 3-nitrobenzyl alcohol as the matrix. Spectra are recorded as:  $m/z$ , assignment, relative intensity (for ions with  $^{56}\text{Fe}$ ). Peaks marked with an asterisk are the strongest of overlapping multiplets related to the assigned formulation by addition or loss of one or two H atoms.

### *Preparation of $\text{Fe}(\overline{\text{C}=\text{CFCF}_2\text{CF}_2})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$*

A solution of  $\text{Na}[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  (11.3 mmol), prepared from  $\{\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\}$

$C_5H_5\}}_2$  (2.0 g, 5.65 mmol) and 1% Na/Hg amalgam (4 ml) in THF (50 ml), was syringed into a Carius tube. Perfluorocyclobutene (2.97 g, 18.33 mmol) was condensed into the tube and after sealing, the contents were stirred at 25 °C for 20 h. After removal of excess  $C_4F_6$  the orange solution was filtered through a Celite pad and the solvent removed from the filtrate at 5 °C under reduced pressure. The residue was chromatographed (Florisil, petroleum spirit eluent) and a major orange band was collected and crystallised (petroleum spirit) to give pale yellow  $Fe(\overline{C=CFCF_2CF_2})(CO)_2(\eta-C_5H_5)$  (**1a**) (2.4 g, 66%) m.p. 50–52 °C. IR:  $\nu(CO)$  (cyclohexane) 2052s, 2007s  $cm^{-1}$  [Lit. [1] m.p. 50–51 °C; IR  $\nu(CO)$  (cyclohexane) 2055s, 2012s  $cm^{-1}$ ].  $^1H$  NMR:  $\delta$  ( $CDCl_3$ ) 5.09 (s,  $C_5H_5$ ).  $^{13}C$  NMR:  $\delta$  ( $CH_2Cl_2$ ) 85.2 (s,  $C_5H_5$ ), 116.9 (tdt,  $^1J(CF)$  286,  $^3J(CF)$  27,  $^2J(CF)$  25 Hz, C(4)), 122.8 (tdt,  $^1J(CF)$  278,  $^2J(CF)$  63,  $^3J(CF)$  21 Hz, C(3)), 147.2 (m,  $J(av)$  7.6 Hz, C(1)), 170.8 (dt,  $^1J(CF)$  326,  $^2J(CF)$  31,  $^3J(CF)$  24 Hz, C(2)), 212.1 (s, CO).  $^{19}F$  NMR:  $\delta$  ( $CS_2$ ) –111.0 (dt,  $^3J(FF)$  24.5,  $^3J(FF)$  22.8 Hz, F(2,3)), –114.1 (tt,  $^3J(FF)$  24.9,  $^4J(FF)$  5.1 Hz, F(1)), –114.9 (td,  $^3J(FF)$  22.8,  $^4J(FF)$  4.8 Hz, F(4,5)).  $\delta$  ( $CH_2Cl_2$ ) –111.9 (m, 2F, F(2,3)), –116.0 (m, 3F, F(1,4,5)).

*Reactions of  $Fe(\overline{C=CFCF_2CF_2})(CO)_2(\eta-C_5H_5)$*

(a) *With  $CH_3CN$ .* Irradiation (400 W, pyrex-filtered) of a solution of  $Fe(\overline{C=CFCF_2CF_2})(CO)_2(\eta-C_5H_5)$  (320 mg, 1.0 mmol) in  $CH_3CN$  (50 ml) with  $N_2$  purge produced an orange solution after 1 h. At this stage the IR spectrum indicated completion of the photolysis (decrease in 2047, 1999  $cm^{-1}$ , increase in 1966  $cm^{-1}$  bands). After decanting the solution into a Schlenk tube, solvent was removed at 0 °C under reduced pressure leaving a viscous orange liquid (327 mg, 98%) which was used for subsequent reactions. For analytical purposes the sample was purified by thin layer chromatography (TLC) (3/2 petroleum spirit/ $CH_2Cl_2$ ). A major orange band ( $R_f$  0.37) was separated from three trace bands. Removal of  $CH_2Cl_2$  from the extract (reduced pressure, 0 °C) left an unstable oil characterised as  $Fe(\overline{C=CFCF_2CF_2})(CO)(NCMe)(\eta-C_5H_5)$  (**1b**) (234 mg, 70%), b.p. 65 °C/10 $^{-1}$  mmHg. Anal. Found: C, 42.94; H, 2.48; N, 3.56;  $M^+$  (FAB MS) 333.  $C_{12}H_8F_5FeON$  calc: C, 43.28; H, 2.42; N, 4.21%;  $M$  333. IR ( $CH_3CN$ ):  $\nu(CO)$  1966s; (neat oil): 1970vs;  $\nu(CH)$  3420(m,br), 3130w, 2832w;  $\nu(CN)$  2290w;  $\nu(C=C)$  1761w, 1692vw, 1671vw, 1609m;  $\nu(CF)$  1368s, 1258s, 1157m, 1114m, 1070s; other bands at 1012w, 1003w, 929s, 839m, 827m, 787s, 771m, 670w, 839w  $cm^{-1}$ .  $^1H$  NMR:  $\delta$  ( $CD_2Cl_2$ ) 4.68 (s,  $C_5H_5$ ), 2.13 (s,  $CH_3CN$ ).  $^{19}F$  NMR:  $\delta$  ( $CH_2Cl_2$ ) –110.8 (m, 2F, F(2,3)), –115.1 (m, 2F, F(4,5)), –119.7 (m, 1F, F(1)) (broad resonances). FAB MS: 333, [ $M^+$ ], 31; 314, [ $M - F$ ] $^+$ , 51; 305, [ $M - CO$ ] $^+$ , 100; 286, [ $M - F - CO$ ] $^+$ , 42; 245\*, [ $M - F - MeCN$ ] $^+$ , 19; 240\*, [ $M - CO - C_5H_5$ ] $^+$ , 6; 199, [ $FeCF_2(CO)(C_5H_5)$ ] $^+$ , 15; 171, [ $FeCF_2(C_5H_5)$ ] $^+$ , 42; 152, [ $FeF(C_5H_5)$ ] $^+$ , 27; 121, [ $FeC_5H_5$ ] $^+$ , 19.

(b) *UV Irradiation.* (i) *In dichloromethane:* Use of a low power lamp (16 W) to irradiate a  $CH_2Cl_2$  solution of  $Fe(\overline{C=CFCF_2CF_2})(CO)_2(\eta-C_5H_5)$  (200 mg, 0.63 mmol) produced gradual decomposition over 20 h (gradual decrease in  $\nu(CO)$  at 2049, 1999  $cm^{-1}$ ). The only product that could be identified after TLC was starting material.

(ii) *In petroleum spirit:* A pyrex-filtered medium pressure lamp (400 W) was used to irradiate a solution of  $Fe(\overline{C=CFCF_2CF_2})(CO)_2(\eta-C_5H_5)$  (150 mg, 0.47 mmol) in petroleum spirit (50 ml). After 90 min little reaction was observed. Use of an unfiltered source resulted in a 50% reduction in intensity of the  $\nu(CO)$  bands over 60 min. This was accompanied by formation of an intractable brown solid.



(c) *Pyrolysis in xylene.* A solution of  $\text{Fe}(\overline{\text{C}=\text{CFCF}_2\text{CF}_2})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$  (130 mg, 0.4 mmol) in xylene (30 ml) was heated under reflux for 4 h to give a cloudy suspension. After cooling, much intractable solid had deposited; filtration and evaporation gave **1a** (IR, TLC) as the only material remaining.

*Reactions of  $\text{Fe}(\overline{\text{C}=\text{CFCF}_2\text{CF}_2})(\text{CO})(\text{NCMe})(\eta\text{-C}_5\text{H}_5)$  (**1b**)*

(a) *With  $\text{PPh}_3$ .* To  $\text{Fe}(\overline{\text{C}=\text{CFCF}_2\text{CF}_2})(\text{CO})(\text{NCMe})(\eta\text{-C}_5\text{H}_5)$  (327 mg, 0.98 mmol) dissolved in  $\text{CH}_2\text{Cl}_2$  (40 ml) was added  $\text{PPh}_3$  (262 mg, 1.0 mmol). After stirring for 3 h (25 °C) the reaction was judged to be complete (IR, TLC) and the solvent was removed under reduced pressure. TLC of the residue (4/1/1 petroleum spirit/ $\text{CH}_2\text{Cl}_2$ / $\text{Et}_2\text{O}$ ) eluted a major orange band ( $R_f$  0.6) which was crystallised by slow evaporation ( $\text{CH}_2\text{Cl}_2$ , petroleum spirit, MeOH) to give orange crystalline  $\text{Fe}(\overline{\text{C}=\text{CFCF}_2\text{CF}_2})(\text{CO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$  (**1c**) (366 mg, 62%), m.p. 169–170 °C. Anal. Found: C, 60.39; H, 3.63;  $M^+$  (FAB MS) 554.  $\text{C}_{28}\text{H}_{20}\text{F}_5\text{FeOP}$  calc: C, 60.67; H, 3.64%;  $M$  554. IR (cyclohexane):  $\nu(\text{CO})$  1964vs; (Nujol) 1950vs, 1908(sh);  $\nu(\text{C}=\text{C})$  1609m;  $\nu(\text{CF})$  1358s, 1254s, 1183s, 1150m, 1106m, 1091s, 1071s, 1053s; other peaks at 1480 m, 1435s, 1012w, 997w, 928s, 850w, 840w, 831w, 787s, 748s, 702(sh), 697s, 687(sh), 640w  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  ( $\text{CDCl}_3$ ) 7.4–7.2 (m, 15H,  $\text{C}_6\text{H}_5$ ), 4.58 (d, 5H,  $J(\text{PH})$  1 Hz,  $\text{C}_5\text{H}_5$ ).  $^{13}\text{C}$  NMR:  $\delta$  ( $\text{CH}_2\text{Cl}_2$ )  $\delta$  83.9 (s,  $\text{C}_5\text{H}_5$ ), 117.0 (tm,  $^1J(\text{CF})$  287 Hz, C(4)), 123.9 (tm,  $^1J(\text{CF})$  248 Hz, C(3)), 128.6–135.6 (m, Ph), 161.2 (m, C(1)), 170.4 (dm,  $^1J(\text{CF})$  322 Hz, C(2)), 219.9 (d,  $J(\text{CP})$  29 Hz, CO).  $^{31}\text{P}$  NMR:  $\delta$  ( $\text{CH}_2\text{Cl}_2$ ) 75.2 (s,  $\text{PPh}_3$ ).  $^{19}\text{F}$  NMR:  $\delta$  ( $\text{CH}_2\text{Cl}_2$ ) –109.9 (d,  $^3J(\text{FF})$  25.4 Hz, F(2,3)), –116.0 (d,  $^2J(\text{FF})$  187.8 Hz, F(4) or F(5)), –116.5 (t,  $^3J(\text{FF})$  25.4 Hz, F(1)), –117.2 (d,  $^2J(\text{FF})$ , 187.5 Hz, F(5) or F(4));  $\delta$  ( $\text{CS}_2$ ) –108.3 (dm,  $^3J(\text{FF})$  26 Hz, F(2,3)), –114.5 (tm,  $^3J(\text{FF})$  27 Hz, F(1)) overlaps with –114.9 (d,  $^2J(\text{FF})$  185 Hz, F(4) or F(5)), –116.1 (d,  $^2J(\text{FF})$  185 Hz, F(5) or F(4));  $\delta$  ( $\text{C}_6\text{H}_6$ ) –108.6 (m, 2F, F(2,3)), –115.8 (m, 3F, F(1,4,5)). FAB MS: 554,  $[M]^+$ , 16; 535,  $[M - \text{F}]$ , 10; 526,  $[M - \text{CO}]^+$ , 100; 507,  $[M - \text{CO} - \text{F}]^+$ , 3; 461,  $[M - \text{CO} - \text{C}_5\text{H}_5]^+$ , 3; 449,  $[M - \text{CO} - \text{Ph}]^+$ , 6; 383\*,  $[\text{Fe}(\text{PPh}_3)(\text{C}_5\text{H}_5)]^+$ , 24; 368,  $[\text{Fe}(\text{CF}_2)(\text{PPh}_3)]^+$ , 27; 337,  $[\text{FeF}(\text{PPh}_3)]^+$ , 19; 318,  $[\text{Fe}(\text{PPh}_3)]^+$ , 50; 280\*,  $[263 + \text{O}]^+$ , 12; 263\*,  $[M - \text{CO} - \text{PPh}_3]^+$ , 73; 184,  $[\text{FeF}(\text{PPh})]^+$ , 48.

(b) *With CO.* CO was bubbled through a solution of  $\text{Fe}(\overline{\text{C}=\text{CFCF}_2\text{CF}_2})(\text{CO})(\text{NCMe})(\eta\text{-C}_5\text{H}_5)$  (146 mg, 0.44 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 ml) for 8 h. Solvent was removed using a nitrogen stream leaving an orange residue which was chromatographed by TLC (4/1 petroleum spirit/ $\text{CH}_2\text{Cl}_2$ ). A major yellow band ( $R_f$  0.45) was collected and crystallised (petroleum spirit/ $\text{CH}_2\text{Cl}_2$ ) to give  $\text{Fe}(\overline{\text{C}=\text{CFCF}_2\text{CF}_2})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$  (92 mg, 65%) identified by comparison (IR, TLC, FAB MS) with an authentic sample.

(c) *Pyrolysis.* Refluxing a solution of  $\text{Fe}(\overline{\text{C}=\text{CFCF}_2\text{CF}_2})(\text{CO})(\text{NCMe})(\eta\text{-C}_5\text{H}_5)$  (60 mg, 0.18 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 ml) for 90 min produced no reaction (monitored by TLC). Refluxing the same amount of the complex in toluene for 5 min produced much decomposition and a yellow solution. After removal of the solvent (under reduced pressure) the residue was chromatographed (TLC; 3/2 petroleum spirit/ $\text{CH}_2\text{Cl}_2$ ) to give a yellow band which was isolated and identified (FAB MS) as  $\text{Fe}(\overline{\text{C}=\text{CFCF}_2\text{CF}_2})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ .

*Crystal structure determinations*

Intensity data for complexes **1a** and **1c** were measured at room temperature on an

Table 2

Crystal data for **1a** and **1c**

	<b>1a</b>	<b>1c</b>
formula	C <sub>11</sub> H <sub>5</sub> F <sub>5</sub> FeO <sub>2</sub>	C <sub>28</sub> H <sub>20</sub> F <sub>5</sub> FeOP
fw	320.0	554.3
crystal system	monoclinic	triclinic
space group	$P2_1/n$ ( $C_{2h}^2$ , No. 14)	$P\bar{1}$ ( $C_1^1$ , No. 2)
$a$ , Å	6.437(1)	9.358(8)
$b$ , Å	15.864(4)	14.890(5)
$c$ , Å	11.585(3)	17.865(4)
$\alpha$ , °	90	103.37(3)
$\beta$ , °	96.54(2)	95.06(4)
$\gamma$ , °	90	91.13(5)
$V$ , Å <sup>3</sup>	1175.3	2410.4
$Z$	4	4
$\rho_c$ , g cm <sup>-3</sup>	1.809	1.527
$F(000)$	632	1104
$\mu$ , cm <sup>-1</sup>	13.00	7.08
max./min. transmission factors	not applied	0.9159, 0.7272
$\theta$ limits, °	1.0–22.5	1.5–21.0
no. of data collected	1822	6881
no. of unique data	1531	6272
data used with $I \geq 2.5\sigma(I)$	766	2472
$R$	0.041	0.072
$k$	0.18	2.25
$g$	0.016	0.002
$R_w$	0.045	0.076
$\rho_{max}$ , eÅ <sup>-3</sup>	0.28	1.03

Table 3

Fractional atomic coordinates ( $\times 10^5$  for Fe;  $\times 10^4$  for remaining atoms) for Fe( $\overline{C=CFCF_2CF_2}$ )(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>) (**1a**)

Atom	$x$	$y$	$z$
Fe	852(19)	13932(8)	22985(10)
F(1)	-2466(11)	370(4)	4668(5)
F(2)	-1408(13)	-1454(4)	3804(7)
F(3)	-4483(11)	-1078(4)	3082(7)
F(4)	117(12)	-886(4)	1883(7)
F(5)	-2971(13)	-472(4)	1197(5)
O(1)	-2380(13)	2411(5)	3724(7)
O(2)	-2808(12)	1535(6)	196(6)
C(1)	-1231(13)	371(6)	2769(7)
C(2)	-2056(16)	58(6)	3664(8)
C(3)	-2492(18)	-807(7)	3234(9)
C(4)	-1561(17)	-472(6)	2169(8)
C(5)	-1409(15)	1996(7)	3155(9)
C(6)	-1721(15)	1468(6)	1027(7)
C(7)	2857(17)	1577(9)	3336(10)
C(8)	2626(20)	2201(8)	2560(17)
C(9)	2530(19)	1818(17)	1424(15)
C(10)	2751(18)	933(12)	1671(14)
C(11)	2955(16)	820(9)	2818(12)

Table 4

Fractional atomic coordinates ( $\times 10^5$  for Fe;  $\times 10^4$  for remaining atoms) for  $\text{Fe}(\overline{\text{C}=\text{CFCF}_2\text{CF}})_2(\text{CO})\text{-}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$  (**1c**)

Atom	x	y	z
Fe(1A)	12199(21)	-15189(13)	-27036(11)
Fe(1B)	-4832(21)	62974(13)	20557(12)
P(1A)	3262(4)	-1301(2)	-3184(2)
P(1B)	1736(4)	5861(2)	1847(2)
O(1A)	2380(12)	-2778(7)	-1820(6)
O(1B)	544(12)	8196(7)	2573(8)
F(1A)	2011(12)	-819(6)	-593(5)
F(2A)	-200(12)	-551(7)	-895(6)
F(3A)	2679(12)	1009(7)	-303(5)
F(4A)	477(11)	1273(6)	-651(5)
F(5A)	2382(11)	1027(5)	-2054(5)
F(1B)	429(15)	4614(7)	3254(7)
F(2B)	-1683(15)	4850(9)	3274(8)
F(3B)	943(14)	5795(9)	-5290(7)
F(4B)	-1281(14)	5939(8)	-5316(6)
F(5B)	348(16)	7512(7)	4097(6)
C(1A)	1480(15)	-450(10)	-1823(8)
C(2A)	1198(18)	-346(11)	-1016(9)
C(3A)	1593(18)	691(11)	-853(9)
C(4A)	1860(18)	455(10)	-1663(9)
C(5A)	-116(17)	-2507(12)	-3519(10)
C(6A)	-726(19)	-2239(13)	-2854(11)
C(7A)	-974(19)	-1319(13)	-2725(11)
C(8A)	-370(19)	-978(13)	-3337(11)
C(9A)	166(18)	-1758(12)	-3843(11)
C(10A)	1928(15)	-2251(10)	-2164(9)
C(11A)	4226(8)	-2348(5)	-3574(4)
C(12A)	5623(8)	-2270(5)	-3774(4)
C(13A)	6354(8)	-3062(5)	-4069(4)
C(14A)	5689(8)	-3933(5)	-4163(4)
C(15A)	4292(8)	-4012(5)	-3963(4)
C(16A)	3560(8)	-3219(5)	-3669(4)
C(17A)	3057(8)	-748(5)	-4000(5)
C(18A)	3294(8)	-1223(5)	-4745(5)
C(19A)	3042(8)	-801(5)	-5362(5)
C(20A)	2553(8)	96(5)	-5234(5)
C(21A)	2316(8)	571(5)	-4489(5)
C(22A)	2568(8)	149(5)	-3871(5)
C(23A)	4656(9)	-585(5)	-2518(4)
C(24A)	5522(9)	53(5)	-2750(4)
C(25A)	6609(9)	564(5)	-2232(4)
C(26A)	6829(9)	437(5)	-1482(4)
C(27A)	5962(9)	-202(5)	-1250(4)
C(28A)	4876(9)	-713(5)	-1767(4)
C(1B)	-275(13)	6117(9)	3071(9)
C(2B)	-402(18)	5331(10)	3451(10)
C(3B)	-165(19)	5948(12)	4246(9)
C(4B)	-111(18)	6655(11)	3837(10)
C(5B)	-1399(17)	5563(11)	956(9)
C(6B)	-1918(15)	5176(10)	1535(9)
C(7B)	-2675(16)	5885(10)	2022(9)
C(8B)	-2568(17)	6681(11)	1752(10)
C(9B)	-1824(16)	6492(11)	1095(9)

continued

Table 4 (continued)

Atom	x	y	z
C(10B)	173(15)	7433(11)	2366(9)
C(11B)	2441(7)	6190(5)	1023(4)
C(12B)	1742(7)	6844(5)	693(4)
C(13B)	2357(7)	7180(5)	123(4)
C(14B)	3672(7)	6861(5)	-117(4)
C(15B)	4372(7)	6207(5)	212(4)
C(16B)	3756(7)	5871(5)	783(4)
C(17B)	3096(8)	6416(5)	2635(4)
C(18B)	3959(8)	7159(5)	2561(4)
C(19B)	4988(8)	7576(5)	3160(4)
C(20B)	5155(8)	7250(5)	3833(4)
C(21B)	4292(8)	6506(5)	3907(4)
C(22B)	3262(8)	6089(5)	3308(4)
C(23B)	2190(8)	4626(5)	1663(4)
C(24B)	3494(8)	4344(5)	1954(4)
C(25B)	3804(8)	3410(5)	1783(4)
C(26B)	2810(8)	2759(5)	1321(4)
C(27B)	1506(8)	3041(5)	1030(4)
C(28B)	1196(8)	3975(5)	1201(4)

Enraf-Nonius CAD4F diffractometer fitted with Mo- $K_{\alpha}$  radiation ( $\lambda$  0.7107 Å). For **1a** significant decomposition of the crystal (ca. 25%) occurred during the data collection and the intensity data set was corrected for this variation; no decomposition of **1c** occurred. Both data sets were corrected for Lorentz and polarisation effects [9] and an absorption correction was applied for **1c**. Relevant crystal data are listed in Table 2.

The structures were solved by normal heavy atom methods and each refined by a full-matrix least-squares procedure based on  $F$  [9]. For **1a**, non-hydrogen atoms were refined anisotropically as for **1c** except that in the latter refinement, the phenyl rings were refined as rigid hexagonal groups. In both models hydrogen atoms were included at their calculated positions. A weighting scheme,  $w = k/[\sigma^2(F) + gF^2]$ , was applied in each case and the refinements continued until convergence. No special features were noted in the analysis of variance for either structure indicating that an appropriate weighting scheme had been applied in each case. Final refinement details are summarised in Table 2. Scattering factors for neutral Fe (corrected for  $f'$  and  $f''$ ) were from ref. [10] and values for the remaining atoms were those incorporated in SHELX [9]. Data solution and refinement were performed with the SHELX programme system on the University of Adelaide's VAX 11/785 computer system.

Fractional atomic coordinates for **1a** and **1c** are listed in Tables 3 and 4 respectively, and the atom numbering schemes employed are shown in Figs. 2 and 3. Listings of thermal parameters, hydrogen atom parameters, all bond distances and angles, and the observed and calculated structure factors may be obtained from the authors.

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