

## Crystal Structure of a Cobalt Carbonyl Complex of 2,2'-Dimethylarsino-octafluoro-1,1'-bicyclobut-1-enyl. A New Rearrangement Product of the Ligand $(\text{Me}_2\text{As})\text{C}:\text{C}(\text{Me}_2\text{As})\text{CF}_2\cdot\text{CF}_2$

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Heating  $\text{Co}_2(\text{CO})_8(\text{f}_4\text{fars})$  [ $\text{f}_4\text{fars} = \text{Me}_2\text{As}\cdot\text{C}:\text{C}(\text{AsMe}_2)\cdot\text{CF}_2\cdot\text{CF}_2$ ] under reflux in hexane has resulted in the cleavage of a  $\text{Me}_2\text{As}$  group from  $\text{f}_4\text{fars}$  with subsequent dimerization of the cyclobutenyl residues to form  $\{(\text{Me}_2\text{As})\text{C}:\text{C}(\text{CF}_2\cdot\text{CF}_2)_2(\text{Me}_2\text{As})\}_2\text{Co}_4(\text{CO})_9(\text{H})_2$ . Crystals are orthorhombic, space group  $C222_1$ , with  $Z = 4$  in a cell of dimensions:  $a = 16.797(3)$ ,  $b = 10.744(3)$  and  $c = 20.559(3)$  Å. X-Ray diffraction data was collected by counter methods, and the structure solved by the tangent refinement technique and refined by full-matrix least-squares procedures to  $R0.041$  for 566 observed reflections. The molecule has a crystallographic two-fold axis which bisects the bond linking the fluorocyclobutenyl groups and the Co-Co bond [2.450(9) Å]. A carbonyl group bridging this bond also lies on the axis. One cobalt atom has a very distorted octahedral environment formed by the  $\pi$ -bond of a fluorocyclobutenyl ring [1.90(3) Å], a terminal carbonyl group, a postulated hydrogen atom, and a dimethylarsine group [Co-As 2.333(6) Å], which is also linked to the second type of cobalt atom [Co-As 2.391(5) Å]; this latter has a trigonal bipyramidal environment with axial (bridging) dimethylarsine and carbonyl groups and equatorial terminal carbonyl groups (two) and the arsenic atom attached to the fluorocyclobutenyl ring [Co-As 2.323(6) Å].

LIGANDS of the type  $\text{CD}^1:\text{CD}^2\text{[CF}_2\text{]}_n\cdot\text{CF}_2$  ( $\text{D}^1 = \text{D}^2 = \text{Me}_2\text{As}$ ,  $n = 1$ ,  $\text{f}_4\text{fars}$ ;  $\text{D}^1 = \text{D}^2 = \text{Ph}_2\text{P}$ ,  $n = 1$ ,  $\text{f}_4\text{fos}$ ,  $n = 2$ ,  $\text{f}_8\text{fos}$ ,  $n = 3$ ,  $\text{f}_8\text{fos}$ ;  $\text{D}^1 = \text{Ph}_2\text{P}$ ,  $\text{D}^2 = \text{Me}_2\text{As}$ ,  $n = 1$ ,  $\text{f}_4\text{asp}$ ) have three potential donor sites, viz. each Group V atom and the ethylene-type linkage, and transition-metal complexes are known in which one, two, or all three donor-sites are utilized.<sup>1</sup> The modes of coordination can be either dentate or bridging; e.g. in  $(\text{f}_4\text{fars})\text{Fe}(\text{CO})_4$ ,  $(\text{f}_4\text{fars})\text{Fe}(\text{CO})_3$ , and  $(\text{f}_4\text{fars})\text{Fe}_2(\text{CO})_8$ ,  $\text{f}_4\text{fars}$  functions as a uni-, a bi-dentate, and a bridging group respectively.<sup>1a</sup> In  $(\text{f}_4\text{fars})\text{Fe}_2(\text{CO})_8$ , the arsenic atoms chelate to one iron atom while the double bond of the cyclobutene group is co-ordinated to the other.<sup>1b,2c</sup> A number of crystal structure analyses<sup>2</sup> and extensive spectra results have confirmed these modes of bonding.

Although the complexes are air-stable at room temperature, both as solids and in solution, it has been found that cleavage reactions can occur when they are heated under reflux;  $(\text{f}_4\text{fars})\text{Fe}_3(\text{CO})_{10}$ , when heated under reflux in cyclohexane, yields a product of empirical formula  $(\text{f}_4\text{fars})\text{Fe}_3(\text{CO})_9$ .<sup>1c</sup> A crystal structure analysis<sup>3</sup>

shows that one  $\text{Me}_2\text{As}$  group has been cleaved from the cyclobutenyl moiety and bridges two iron atoms; the cyclobutenyl residue co-ordinates to each of two iron atoms *via* the arsenic atom and the ethylene linkage while a carbon-iron  $\sigma$ -bond is formed by the carbon atom at the point of cleavage and the third iron atom. A similar type cleavage occurs when  $(\text{f}_4\text{fars})\text{Mn}_2(\text{CO})_8$  is heated under reflux in xylene; however, there is no linkage involving the double bond of the cyclobutene ring.<sup>4,5a,b</sup>

When  $(\text{f}_4\text{fars})\text{Co}_2(\text{CO})_8$  is heated under reflux in hexane, a compound of empirical formula  $(\text{f}_4\text{fars})_2\text{Co}_4(\text{CO})_9(2\text{H}?)$  is formed.<sup>5b</sup> This structure analysis shows that an  $\text{Me}_2\text{As}$  group has been cleaved from  $\text{f}_4\text{fars}$  and that two cyclobutenyl residues dimerize to form a new bicyclobutenyl species.

<sup>1</sup> (a) W. R. Cullen, D. A. Harbourn, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, 1969, **8**, 95; (b) *ibid.*, p. 1464; (c) *ibid.*, 1970, **9**, 702; (d) W. R. Cullen and D. A. Harbourn, *ibid.*, p. 1839; (e) W. R. Cullen, P. S. Dhaliwal, and C. J. Stewart, *ibid.*, 1967, **6**, 2256; (f) J. P. Crow and W. R. Cullen, *ibid.*, 1971, **10**, 1529; (g) *ibid.*, p. 2165; (h) W. R. Cullen and J. A. J. Thompson, *Canad. J. Chem.*, 1970, **48**, 1730; (i) W. R. Cullen, D. F. Dong, and J. A. J. Thompson, *ibid.*, 1969, **47**, 4671.

<sup>2</sup> (a) P. J. Roberts and J. Trotter, *J. Chem. Soc. (A)*, 1971, 1479; (b) W. Harrison and J. Trotter, *ibid.*, p. 1607; (c) P. J. Roberts and J. Trotter, *ibid.*, 1970, 3246; (d) P. J. Roberts, B. R. Penfold, and J. Trotter, *Inorg. Chem.*, 1970, **9**, 2137; (e) F. W. B. Einstein and J. Trotter, *J. Chem. Soc. (A)*, 1967, 824; (f) F. W. B. Einstein and R. D. G. Jones, *ibid.*, 1971, 3359; (g) *idem.*, preceding paper; (h) F. W. B. Einstein and R. D. G. Jones, *Inorg. Chem.*, in press; (i) L. Y. Y. Chan and F. W. B. Einstein, to be published; (j) F. W. B. Einstein and C. R. S. M. Hampton, *Canad. J. Chem.*, 1971, **49**, 1901.

<sup>3</sup> F. W. B. Einstein, Anne-Marie Pilotti, and R. Restivo, *Inorg. Chem.*, 1971, **10**, 1947.

<sup>4</sup> J. P. Crow, W. R. Cullen, F. L. Hou, L. Y. Y. Chan, and F. W. B. Einstein, *Chem. Comm.*, 1971, 1229.

<sup>5</sup> (a) F. W. B. Einstein and A. C. MacGregor, to be published; (b) W. R. Cullen, personal communication.

## EXPERIMENTAL

The compound crystallized as dark green plates with the longest direction parallel to  $b$ . Weissenberg photographs of nets  $h0-3l$ , and precession photographs of nets  $hk0-1$  and  $0-1kl$ , taken with  $\text{Cu-K}\alpha$  radiation, indicated the crystals were orthorhombic.

*Crystal Data.*— $\text{C}_{25}\text{H}_{28}\text{As}_4\text{Co}_4\text{F}_8\text{O}_9$ ,  $M = 1155.8$ , Orthorhombic,  $a = 16.797(3)$ ,  $b = 10.744(3)$ ,  $c = 20.559(3)$  Å,  $U = 3710$  Å<sup>3</sup>,  $D_m = 1.93(7)$  (Bermann density balance),  $Z = 4$ ,  $D_c = 2.06$ ,  $F(000) = 2232$ .  $\lambda(\text{Mo-K}\alpha) = 0.70926$ ,  $\lambda(\text{Mo-K}\alpha) = 0.7107$  Å,  $\mu(\text{Mo-K}\alpha) = 56.2$  cm<sup>-1</sup>. Space group  $C22_2$  from systematic absences:  $hkl$  when  $h + k$  is odd,  $00l$  when  $l$  is odd.

In the very small sample available, most crystals grew as thin plates. The thickest crystal ( $ca.$   $0.35 \times 0.26 \times 0.16$  mm along  $b$ ,  $a$ , and  $c$  respectively) was used for the measurement of cell dimensions and for data collection. It was aligned with the  $b^*$  axis coincident with  $\phi$  and the variation in intensity of  $0,2,0$  with  $\phi$  was determined. The variation amount to 20% of the maximum value. Cell dimensions were obtained by the least-squares analysis of  $2\theta$  values for 19 reflections ( $2\theta > 23^\circ$ ) which had been automatically centred on a computer-controlled, Picker four-circle diffractometer,\* with  $\text{Mo-K}\alpha$  radiation, and a take-off angle of  $1^\circ$ . Errors in the cell dimensions were determined by the least-squares process.

Intensity data for one octant were collected by the  $\theta-2\theta$  scan technique by use of  $\text{Mo-K}\alpha$  radiation (niobium filter) and a scintillation counter with pulse-height analysis. In order to minimize intrinsic multiple reflection,  $b^*$  was offset slightly from the  $\phi$  axis. The take-off angle was  $3^\circ$ , the detector was positioned 28 cm from the crystal and the detector aperture was 5 mm high and 4 mm wide. Each reflection was scanned for  $1.1^\circ$  in  $2\theta$  (extended for spectral dispersion) at a scan rate of  $2^\circ \text{ min}^{-1}$ . At each end of the scan range, a stationary background count was made for 10s. Every 50 reflections, two standard reflections were monitored and the maximum deviation of any standard from the mean was 5%. In this manner, intensities for 1006 reflections with  $2\theta \leq 40^\circ$  were measured. Because of the large fraction of reflections whose intensities were not significantly above background, data was not collected beyond this range.

Intensities were corrected for background (normalized for the scan time), variation of the standard reflections, and the Lorentz-polarization factor. A correction was made for absorption as a function of  $\phi$ .<sup>6</sup> If the net count for a reflection was  $< 2\sigma$ ,  $\sigma = (\text{total count} + \text{background})^{1/2}$ , the reflection was considered unobserved. The number of observed reflections was 566.

*Structure and Determination.*—Structure solution was initiated by the tangent refinement procedure.<sup>7</sup>  $E$  Values were calculated and reflections  $5,7,0$  ( $2.50, 0$ ),  $0,6,7$  ( $2.45, 0$ ) and  $4,0,5$  ( $3.00, \pi/2$ ) were chosen to define the origin and enantiomorph. In addition, inspection allowed the assignment of phases to  $0,0,10$  ( $2.64, 0$ ) and  $10,0,0$  ( $2.37, 0$ ) which aided initial phase assignment for the high  $E$  values. After 6 cycles of tangent refinement, phases had been determined for all reflections with  $E \geq 1.5$  and  $R_K \dagger$  was  $0.15$ . From

\* Computer programs for diffractometer control and preliminary calculations were written by Dr. P. G. Lenhart. All other programs for calculation are as described in F. W. B. Einstein and R. D. G. Jones, *J. Chem. Soc. (A)*, 1971, 3359.

†  $R_K = (\sum |E_h|_o - |E_h|_c) / \sum |E_h|_o$ ; see ref. 7 (a).

‡  $R' = \{\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2\}^{1/2}$ .

an  $E$  map, four positions were selected which were consistent with reasonable cobalt and arsenic positions and the major features of a Patterson synthesis. These four positions were related to an equivalent set of four by a two-fold axis along  $(x,0,0)$  such that the two-fold axis bisects a cobalt-cobalt bond. The remaining non-hydrogen atomic positions were derived from subsequent Fourier syntheses. Refinement of positional and isotopic temperature parameters by the full-matrix least-squares method, assigning each reflection unit weight, gave  $R$  0.055. The function

TABLE 1

Final atomic parameters: fractional co-ordinates and isotropic thermal parameters with estimated standard deviations in parentheses

Atom	$x$	$y$	$z$	$B_{\text{iso}}/\text{Å}^2$
As(1)	0.2933(3) *	0.2156(3)	0.3747(1)	*
As(2)	0.1061(2)	0.1909(3)	0.3910(2)	*
Co(3)	0.1597(3)	0.1113(4)	0.4871(2)	*
Co(4)	0.1944(3)	0.1605(4)	0.3012(2)	*
F(15)	0.382(1)	0.292(2)	0.508(1)	*
F(16)	0.266(1)	0.352(2)	0.541(1)	*
F(13)	0.380(1)	0.101(2)	0.581(1)	6.5(5)
F(14)	0.266(1)	0.144(2)	0.618(1)	6.3(5)
C(5)	0.404(3)	0.169(4)	0.357(2)	6.4(10)
C(6)	0.307(2)	0.395(4)	0.383(2)	5.9(9)
C(7)	0.003(2)	0.124(4)	0.363(2)	5.7(9)
C(8)	0.078(2)	0.369(3)	0.400(2)	4.6(9)
C(9)	0.272(2)	0.172(3)	0.468(2)	3.8(7)
C(10)	0.273(2)	0.062(2)	0.504(1)	1.9(6)
C(11)	0.303(3)	0.132(3)	0.558(2)	5.3(8)
C(12)	0.311(2)	0.255(4)	0.517(2)	5.1(9)
C(17)	0.118(2)	0.214(4)	0.539(2)	6.0(10)
O(18)	0.089(2)	0.296(4)	0.569(2)	10.8(10)
C(19)	0.079(4)	0.0	0.5	6.5(15)
O(20)	0.007(3)	0.0	0.5	8.6(11)
C(21)	0.264(2)	0.146(4)	0.242(2)	6.7(11)
O(22)	0.314(2)	0.123(3)	0.202(1)	7.0(7)
C(23)	0.154(2)	0.015(4)	0.296(2)	4.8(8)
O(24)	0.129(2)	-0.089(3)	0.289(1)	6.5(7)
C(25)	0.148(2)	0.283(4)	0.261(2)	4.6(8)
O(26)	0.111(2)	0.364(3)	0.238(1)	6.8(7)

\* Anisotropic temperature factors in (Å<sup>2</sup>) in the form  $\exp -2\pi(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)$

Atom	$10^3 U_{11}$	$10^3 U_{22}$	$10^3 U_{33}$	$10^3 U_{12}$	$10^3 U_{13}$	$10^3 U_{23}$
As(1)	49(2)	46(2)	32(2)	-7(2)	1(2)	1(2)
As(2)	40(2)	50(2)	35(2)	3(2)	2(2)	3(2)
Co(3)	44(2)	43(3)	38(3)	4(3)	9(2)	2(3)
Co(4)	51(3)	48(3)	30(2)	-2(3)	3(3)	1(2)
	$10^2 U_{11}$	$10^2 U_{22}$	$10^2 U_{33}$	$10^2 U_{12}$	$10^2 U_{13}$	$10^2 U_{23}$
F(15)	12(2)	14(2)	6(1)	-11(2)	-3(1)	5(2)
F(16)	15(2)	6(1)	5(1)	-1(1)	2(1)	-3(1)

minimized was  $\sum w(|F_o| - |F_c|)^2$ . In an electron-density difference synthesis, the major features were consistent with anisotropic thermal motion for arsenic and cobalt atoms, F(15) and F(16) and incorporation of appropriate variables caused refinement to converge to an  $R$  and  $R'$  of  $0.041$  and  $0.052$ .<sup>‡</sup> The parameter shifts in the last cycle were  $< 0.1\sigma$ . The weighting scheme was as described previously<sup>8</sup> with  $A = 39$ ,  $B = 100$ , and  $C = 130$  and the error of fit was  $1.17$ . This weighting scheme yielded  $w(|F_o| - |F_c|)^2$  constant for ranges of  $F_o$  and  $\sin \theta \lambda^{-1}$ , and having no dependence on the

<sup>6</sup> A. C. T. North, D. C. Phillips, and F. S. Matthews, *Acta Cryst.*, 1968, **A**, 24, 361.

<sup>7</sup> (a) J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849; (b) J. Karle, *Acta Cryst.*, 1968, **B**, 24, 182.

<sup>8</sup> F. W. B. Einstein and R. D. G. Jones, *J. Chem. Soc. (A)*, 1971, 2762.

$\phi$  angle, indicating that the absorption correction was reasonable. A final electron-density difference map had a number of peaks and troughs of maximum density 0.47

TABLE 2  
Interatomic distances and angles

## (a) Interatomic distances (Å)

Co(3)—Co(3')	2.450(9)	As(1)—C(5)	1.96(4)
Co(3)—C(17)	1.69(4)	As(1)—C(6)	1.95(4)
Co(3)—C(19)	1.83(4)	As(1)—C(9)	2.00(3)
Co(3)— $x$	1.90(3)	As(2)—C(7)	1.96(4)
Co(4)—C(21)	1.70(4)	As(2)—C(8)	1.97(4)
Co(4)—C(23)	1.71(4)	C(9)—C(10)	1.40(4)
Co(4)—C(25)	1.74(4)	C(9)—C(12)	1.50(4)
Co(4)—As(1)	2.323(6)	C(10)—C(11)	1.43(4)
Co(4)—As(2)	2.391(5)	C(11)—C(12)	1.57(5)
Co(3)—As(2)	2.333(6)	C(10)—C(10')	1.34(6)
C(17)—O(18)	1.17(4)	C(11)—F(13)	1.42(4)
C(19)—O(20)	1.21(6)	C(11)—F(14)	1.40(4)
C(21)—O(22)	1.19(4)	C(12)—F(15)	1.28(4)
C(23)—O(24)	1.20(4)	C(12)—F(16)	1.37(4)
C(25)—O(26)	1.16(4)		

## (b) Interatomic angles (deg.)

Co(4)—As(1)—C(5)	120(1)	As(2)—Co(4)—C(21)	175(2)
Co(4)—As(1)—C(6)	113(1)	As(2)—Co(4)—C(23)	86(1)
Co(4)—As(1)—C(9)	116(1)	As(2)—Co(4)—C(25)	89(1)
C(5)—As(1)—C(6)	99(2)	C(21)—Co(4)—C(23)	98(2)
C(5)—As(1)—C(9)	106(1)	C(21)—Co(4)—C(25)	92(2)
C(6)—As(1)—C(9)	100(1)	C(23)—Co(4)—C(25)	119(2)
Co(4)—As(2)—Co(3)	111.4(2)	Co(3)—C(7)—O(18)	171(4)
Co(4)—As(2)—C(7)	106(1)	Co(3)—C(19)—O(20)	138(1)
Co(4)—As(2)—C(8)	111(1)	Co(4)—C(21)—O(22)	173(4)
Co(3)—As(2)—C(7)	117(1)	Co(4)—C(23)—O(24)	175(3)
Co(3)—As(2)—C(8)	111(1)	Co(4)—C(25)—O(26)	174(3)
C(7)—As(2)—C(8)	100(2)	As(1)—C(9)—C(10)	135(2)
As(2)—Co(3)—Co(3')	122.8(3)	As(1)—C(9)—C(12)	115(2)
As(2)—Co(3)— $x$	111(1)	C(9)—C(10)—C(11)	88(2)
As(2)—Co(3)—C(17)	98(1)	C(10)—C(11)—C(12)	94(3)
As(2)—Co(3)—C(19)	94(1)	C(11)—C(12)—C(9)	80(3)
Co(3')—Co(3)— $x$	92(1)	C(9)—C(10)—C(10')	140(4)
Co(3')—Co(3)—C(17)	120(1)	C(11)—C(10)—C(10')	129(3)
Co(3')—Co(3)—C(19)	48(1)	C(10)—C(11)—F(13)	117(3)
$x$ —Co(3)—C(17)	114(1)	C(10)—C(11)—F(14)	125(3)
$x$ —Co(3)—C(19)	140(1)	C(12)—C(11)—F(13)	108(3)
C(17)—Co(3)—C(19)	91(2)	C(12)—C(11)—F(14)	116(3)
As(1)—Co(4)—As(2)	84.6(2)	F(13)—C(11)—F(14)	97(3)
As(1)—Co(4)—C(21)	90(1)	C(9)—C(12)—F(15)	119(3)
As(1)—Co(4)—C(23)	124(1)	C(9)—C(12)—F(16)	117(3)
As(1)—Co(4)—C(25)	116(1)	C(11)—C(12)—F(15)	114(3)
		C(11)—C(12)—F(16)	114(3)
		F(15)—C(12)—F(16)	110(3)

Primed atoms are related to unprimed atoms by a two-fold axis at ( $X$ , 0, 0);  $x$  is the mid-point of C(9)—C(10).

and  $-0.46 \text{ eÅ}^{-3}$ , usually near carbonyl groups although some were consistent with methyl hydrogen positions. These densities may be compared with those of a carbon atom, viz. ca.  $5 \text{ eÅ}^{-3}$ .

Scattering factors for the neutral atoms were taken from ref. 9 while anomalous scattering corrections,  $\Delta f'$  and  $\Delta f''$ , for arsenic and cobalt were from ref. 10.

Final atomic parameters and interatomic distances and

\* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

<sup>9</sup> D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

<sup>10</sup> 'International Tables for X-Ray Crystallography,' vol. III, 1962, Kynoch Press, Birmingham, p. 213.

angles are in Tables 1 and 2. The equations for selected planes through atomic groupings are shown in Table 3.

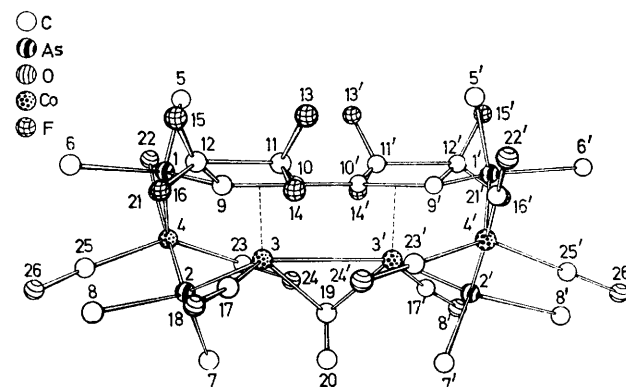
TABLE 3

Equation of selected planes, in the form  $AX + BY + CZ + D = 0$  where  $X$ ,  $Y$ , and  $Z$  are co-ordinates in Å corresponding to directions  $a$ ,  $b$ , and  $c$

Plane (I):	$A$	$B$	$C$	$D$	$\chi^2$
C(9)—(12)	0.9202	-0.2296	-0.3172	-0.7645	3.4
Plane (II):					
As(1), C(23), C(25)	0.6564	-0.1638	-0.7364	2.819	
Plane (III):					
C(9), C(10), C(10'), C(9')	1.000	0.000	0.000	-4.586	0.5

The angle between plane (I) and its two-fold equivalent is  $46^\circ$ .

The Figure illustrates the atomic arrangement in one molecule of the compound.



A diagram of the molecule showing the atom numbering system

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20495 (2 pp., 1 microfiche).\*

## DISCUSSION

The bicyclobutenyl ligand in this compound represents a new rearrangement product of a  $f_4$ fars-metal carbonyls. Previously, when  $\text{Me}_2\text{As}$  has been cleaved from  $f_4$ fars, bonding to the metal atom has taken place from the carbon at the cleaved position <sup>5</sup> and also in some cases, from the ethylene-bridge group.<sup>2a,3,11</sup> However, for the present compound, after  $\text{Me}_2\text{As}$  has been cleaved, dimerization of the cyclobutene residues occurs to form a bicyclobutenyl derivative. Octafluoro-1,1'-bicyclobut-1-ene derivatives in which the 2,2'-positions are occupied by chlorine are known <sup>12</sup> but this represents the first case where Group V atoms are in the 2,2'-positions.

Formulating the correct composition is difficult. If the 'effective atomic number rule' is invoked, Co(4) can obtain the krypton configuration by donation of a total of 9 electrons from As(1), C(21), C(23), C(25), and As(2),

<sup>11</sup> F. W. B. Einstein and R. D. G. Jones, to be published.

<sup>12</sup> J. D. Park, S. K. Choi, and H. E. Romine, *J. Org. Chem.*, 1969, **34**, 2521.

the last-named being a one-electron donor. However, Co(3) will only have 8 electrons donated, As(2) in this case being a two-electron donor (maximum possible). The ninth electron could be gained from a hydrogen atom. Since insufficient sample was available, the  $^1\text{H}$  n.m.r. spectra was not determined; in such compounds, protons of this type have been found difficult to locate. The spatial arrangement of ligands about Co(3) leaves sufficient space *trans* to C(9)–C(10) for a hydrogen atom (a weak peak of height  $0.3 \text{ e}\text{\AA}^3$  was observed at  $1.2 \text{ \AA}$  from the cobalt atom in this area). An alternative scheme, which would imply double-bond character of the Co(3)–Co(3') link, seems inappropriate since the bond length,  $2.450(9) \text{ \AA}$ , is in the range of single-bond distances suggested in other cobalt cluster compounds.<sup>2b,f,h</sup> Although the available evidence is mainly indirect, we suggest that it favours the hydride formulation.

The molecule has a two-fold crystallographic axis which passes through C(19) and O(20) and bisects Co(3)–Co(3') and C(10)–C(10'). Two different types of cobalt are present. With the hydride formulation, the geometry about Co(3) is a very distorted octahedron. Co(3) is bonded to Co(3'), the bridging carbonyl group, a terminal carbonyl group, a cyclobutene moiety, and to As(2) which forms an asymmetric bridging link to Co(4). As(2) and C(21) are the axial groups in the trigonal bipyramid about Co(4), the equatorial plane being formed by As(1) and two terminal carbonyl groups with the Co(4) atom displaced  $0.11 \text{ \AA}$  towards C(21).

Co(4)–As(1) and Co(3)–As(2) are  $2.323(6)$  and  $2.333(6) \text{ \AA}$  whereas Co(4)–As(2),  $2.391(5) \text{ \AA}$ , is significantly longer. Two effects may account for this difference. Muetterties and Schunn<sup>13</sup> have observed that where there are different substituents in a trigonal bipyramidal moiety of a main-group element, bond lengths to atoms of the

same type in equatorial and axial positions show highly significant differences. Although it can be dangerous to extrapolate these results to transition metals, this effect may be contributing to the difference in cobalt–arsenic bond lengths in this compound. The other factor involves the character of the bonding orbitals used by the arsenic atom. Consideration of the angles about As(1) and As(2) indicated enhanced *s* orbital character used by As(1) and As(2) in the bonds to Co(4) and Co(3), respectively, and correspondingly increased *p* character for the others. Consequently, the covalent radii of As(1) and As(2) in the direction of Co(4) and Co(3) are reduced resulting in shorter arsenic–cobalt bond lengths.

The bond from Co(3) to C(9)–C(10) can be described in two ways: one assigns a  $\pi$  bond between Co(3) and the ethylene-type bond, the other describes the system in terms of two cobalt–carbon  $\sigma$  bonds. For the present compound, C(9)–C(10) is  $1.40(4)$ , C(10)–C(10') is  $1.34(6) \text{ \AA}$  and the grouping C(9), C(10), C(10'), C(9') is planar, suggesting the C(9)  $\cdots$  C(9') system is conjugated and that C(9)–C(10) has a large percentage of double-bond character. In addition, Co(3) is  $1.75 \text{ \AA}$  below plane (I) with the Co(3)–(mid-point) C(9)  $\cdots$  C(10) vector approximately at right angles to the plane. As(1) is  $0.79 \text{ \AA}$  above plane (I) but the angle between the plane and the C(9)  $\cdots$  As(1) vector is not large. From this evidence, the  $\pi$  bond formulation seems most appropriate.

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<sup>13</sup> E. L. Muetterties and R. A. Schunn, *Quart. Rev.*, 1966, **20**, 245.