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A Heterometallic Biscarbyne Cluster,* $C_{27}H_{20}Co_2FeO_3$

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Abstract. $M_r = 566.17$, orthorhombic, $Pbca$, $a = 16.660$ (5), $b = 32.106$ (8), $c = 8.598$ (2) Å, $V = 4599$ Å³, $Z = 8$, $D_x = 1.63$ Mg m⁻³, $F(000) = 2288$, $\lambda(\text{Mo } K\alpha) = 0.70926$ Å, $\mu = 1.98$ mm⁻¹, $T = 293$ K. Refinement of 298 variables by full-matrix least-squares methods on F converged at agreement factors $R = 0.043$ and $R_w = 0.033$ using 2220 observations with $F^2 > 3\sigma(F^2)$. The triangular metal cluster formed by the $Fe(CO)_3$ and two $(\eta^5-C_5H_5)Co$ fragments is doubly capped by two $\mu_3\eta^1-C(C_6H_5)$ carbyne ligands derived from diphenylacetylene.

Introduction. As part of an investigation into the construction of heterometallic cluster compounds, we have explored the interchangeability of skeletal components such as $Co(CO)_3$, $(\eta^5-C_5H_5)Ni$ and diphenylacetylene (Freeland, Hux, Payne & Tyers, 1980). Similar approaches have been taken by Beurich & Vahrenkamp (1981), who prepared a heterometallic cluster monocapped with a $\equiv C-C_6H_5$ carbyne ligand, $[\mu_3\eta^1-C(C_6H_5)][(\eta^5-C_5H_5)Ni][Co(CO)_3]_2$, and by Fritch & Vollhardt (1980), who prepared the doubly capped $[\mu_3\eta^1-C(C_6H_5)]_2[(\eta^5-C_5H_5)Co]_3$ from diphenylacetylene and $(\eta^5-C_5H_5)Co(CO)_2$ in 72% yield. In each case the carbyne ligand(s) resulted from alkyne cleavage under the reaction conditions. We too have observed such alkyne cleavage in the formation of the title compound, which appeared as a minor product in all thermal reactions employed to prepare $[(\eta^5-C_5H_5)Ni][Fe(CO)_3][Co(CO)_3]C_2(C_6H_5)_2$ (Einstein, Freeland, Tyers, Sutton & Waterous, 1982). The dark-brown complex was separated by chromatography on Florisil, recrystallized from hexane, and mounted in a capillary under a N_2 atmosphere.

* 3,3,3-Tricarbonyl-1,2-bis(η^5 -cyclopentadienyl)-bis(μ_3 -phenylmethylidyne)-triangulo-dicobaltiron.

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Experimental. Space group $Pbca$, systematic absences k odd for $0kl$, l odd for $h0l$ and h odd for $hk0$. Crystal faces $\{100\}$, $\{010\}$, $\{121\}$, $\{1\bar{1}\bar{1}\}$, $\{1\bar{2}\bar{1}\}$ and $\{1\bar{1}2\}$, approximate dimensions $0.41 \times 0.20 \times 0.03$ mm, $V = 0.0028$ mm³, $\{010\}$ faces well developed. Picker FACS-1 diffractometer, Vanderbilt operating system (Lenhart, 1975). Mo radiation, monochromatized by graphite, cell parameters from 25 reflexions $17^\circ < 2\theta < 28^\circ$, 4489 observations ($+h, +k, +l$) over 16 days by θ - 2θ scan, maximum 2θ 50° . 10 s stationary-crystal, stationary-counter background estimates, 1° , dispersion-corrected, scans for $2 \leq 2\theta \leq 35^\circ$; 20 s backgrounds for $2\theta > 35^\circ$. Standard reflections 200, 040, 200, 111, 102 and 104, average decay 12%, no correction applied. ω -scans (Furnas, 1957) had an average width at half-height of 0.11° before and after data collection. Background, monochromator polarization and Lorentz-polarization corrections applied and standard deviations assigned (Payne, 1973); $p = 0.03$ (Busing & Levy, 1957). Absorption correction by the analytical method [AGNOST (Cahen & Ibers, 1972)]; transmission factors from 0.646 to 0.936. 80 data with $k = \bar{1}$ also recorded; R factors for averaging were 0.021 and 0.020 before and after absorption correction. Solution by Patterson and Fourier techniques. Refinement by full-matrix least-squares methods, minimizing $\sum w(|F_o| - |F_c|)^2$, weight $w = 4F_o^2/\sigma^2(F_o^2)$. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), for H from Stewart, Davidson & Simpson (1965). Anomalous-dispersion contributions for Co and Fe (Cromer & Liberman, 1970). All 20 H atoms located and included in idealized positions (sp^2 hybridization, C-H 0.90 Å) with isotropic Debye factors 10% greater than those of bonded atoms. Convergence [298 variables and 2220 unique observations, $F_o^2 > 3\sigma(F_o^2)$] at $R = 0.043$ and $R_w = 0.033$, $S = 1.84$; $(\Delta/\sigma)_{\max} = 0.2$, final maximum $\Delta\rho$ excursion 0.4 (1) e Å⁻³ (at 0.441, 0.054, 0.163), of no chemical significance. Statistical analysis of R_w ,

showed no unusual trends, no secondary extinction. All computing carried out on the DEC PDP-10 and the CDC Cyber 73-14 at the University of Western Ontario, using programs described in detail elsewhere (Farrar & Payne, 1981). $\sigma(\bar{X})$ values calculated from $[\sum_i(x_i - \bar{x})^2/(n-1)]^{1/2}$. The final positional parameters and their e.s.d.'s are given in Table 1 for non-hydrogen atoms.*

Discussion. A perspective view of the molecule showing the atom-numbering scheme is given in Fig. 1, and an ORTEP stereoview (Johnson, 1965) is shown in Fig. 2. The crystals are built up from discrete molecules, for the shortest intermolecular distances are 2.47 Å between H1C(7) and H1C(27) at $(x, \frac{1}{2}-y, \frac{1}{2}+z)$, and 2.44 Å between H1C(17) and H1C(17) at $(x, 1-y, z)$. Selected intramolecular distances and angles are given in Table 2. Weighted least-squares planes for the cyclopentadienyl and phenyl rings show that all four are planar within experimental error.

The molecule contains a triangular core of metal atoms, doubly capped by two $\equiv\text{C}-\text{C}_6\text{H}_5$ carbyne ligands. The Co—Co distance of 2.366 (2) Å is con-

siderably shorter than the Fe—Co distances of 2.429 (2) and 2.469 (2) Å, and compares well with the average distance of 2.383 (9) Å in $[\mu_3\eta^1\text{-CSi}(\text{CH}_3)_3][\mu_3\eta^1\text{-C}_3\text{Si}(\text{CH}_3)_3][(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_3$ (Fritch, Vollhardt, Thompson & Day, 1979) and those of 2.366 (1), 2.366 (1) and 2.393 (2) Å in $[\mu_3\eta^1\text{-C}(\text{CH}_3)]_3[\mu_3\eta^1\text{-CO}_2\text{CH}_3][(\eta^5\text{-C}_5\text{H}_5)\text{Co}]$ (Yamazaki, Wakatsuki & Aoki, 1979). The mean Co—C(carbyne) distance is

Table 2. Intramolecular bond distances (Å) and angles (°)

Fe—Co(1)	2.469 (2)	Fe—C(1)	1.837 (9)
Fe—Co(2)	2.429 (2)	Fe—C(2)	1.807 (9)
Co(1)—Co(2)	2.366 (2)	Fe—C(3)	1.804 (9)
Co(1)—C(14)	1.872 (7)	C(1)—O(1)	1.117 (9)
Co(2)—C(14)	1.874 (7)	C(2)—O(2)	1.116 (9)
Fe—C(14)	1.989 (7)	C(3)—O(3)	1.133 (9)
Co(1)—C(21)	1.873 (8)	C(14)—C(15)	1.474 (9)
Co(2)—C(21)	1.901 (7)	C(21)—C(22)	1.483 (9)
Fe—C(21)	1.958 (7)		
Co(1)—Fe—Co(2)	57.75 (4)	Co(1)—C(14)—C(15)	126.2 (5)
Fe—Co(1)—Co(2)	60.26 (5)	Co(2)—C(14)—C(15)	138.2 (5)
Co(1)—Co(2)—Fe	61.98 (4)	Fe—C(14)—C(15)	134.2 (5)
Co(1)—C(14)—Co(2)	78.3 (3)	Co(1)—C(21)—C(22)	131.6 (5)
Co(1)—C(14)—Fe	79.5 (3)	Co(2)—C(21)—C(22)	133.5 (6)
Co(2)—C(14)—Fe	77.9 (3)	Fe—C(21)—C(22)	133.8 (6)
Co(1)—C(21)—Co(2)	77.6 (3)	Fe—C(1)—O(1)	178.4 (8)
Co(1)—C(21)—Fe	80.2 (3)	Fe—C(2)—O(2)	176.6 (8)
Co(2)—C(21)—Fe	78.0 (3)	Fe—C(3)—O(3)	176.4 (8)
C(14)—C(15)—C(16)	122.8 (7)	C(1)—Fe—C(2)	93.9 (4)
C(14)—C(15)—C(20)	120.3 (7)	C(1)—Fe—C(3)	97.4 (4)
C(21)—C(22)—C(23)	122.7 (7)	C(2)—Fe—C(3)	100.5 (4)
C(21)—C(22)—C(27)	120.0 (7)		

* Lists of anisotropic thermal parameters, H-atom parameters, additional bond distances and angles, mean-plane calculations and structure amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38762 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10^3$) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq} (Å ²)
Co(1)	3008.0 (6)	3460.3 (3)	476.4 (12)	29.1 (6)
Co(2)	3214.9 (6)	3877.7 (3)	-1755.2 (12)	29.9 (6)
Fe	3994.9 (6)	4033.6 (3)	559.2 (13)	28.9 (6)
O(1)	3754 (4)	4859 (2)	2008 (8)	78 (5)
O(2)	5306 (4)	4317 (2)	-1436 (7)	66 (5)
O(3)	4878 (4)	3627 (2)	3093 (7)	72 (5)
C(1)	3836 (5)	4545 (3)	1471 (10)	46 (6)
C(2)	4818 (5)	4213 (2)	-636 (10)	39 (5)
C(3)	4539 (5)	3796 (3)	2141 (9)	42 (6)
C(4)	2270 (7)	3272 (3)	2291 (12)	62 (7)
C(5)	1862 (6)	3222 (3)	904 (14)	63 (8)
C(6)	2301 (7)	2944 (3)	6 (11)	62 (8)
C(7)	2983 (6)	2815 (2)	845 (12)	54 (7)
C(8)	2959 (6)	3023 (3)	2264 (11)	57 (7)
C(9)	3522 (7)	4243 (3)	-3696 (11)	66 (8)
C(10)	3631 (6)	3805 (4)	-4007 (9)	66 (8)
C(11)	2862 (7)	3611 (3)	-3815 (10)	60 (7)
C(12)	2310 (5)	3922 (3)	-3423 (9)	54 (7)
C(13)	2712 (7)	4311 (3)	-3341 (11)	61 (7)
C(14)	2816 (4)	4030 (2)	202 (7)	27 (4)
C(15)	2136 (5)	4268 (2)	847 (9)	31 (5)
C(16)	1505 (5)	4408 (3)	-57 (9)	48 (6)
C(17)	868 (6)	4617 (3)	625 (13)	66 (7)
C(18)	851 (6)	4699 (3)	2157 (12)	54 (7)
C(19)	1469 (6)	4568 (3)	3071 (10)	55 (7)
C(20)	2102 (5)	4356 (2)	2445 (10)	41 (6)
C(21)	3949 (4)	3525 (2)	-693 (9)	34 (5)
C(22)	4559 (5)	3219 (2)	-1218 (9)	33 (5)
C(23)	5348 (5)	3225 (2)	-695 (9)	37 (5)
C(24)	5875 (5)	2925 (3)	-1168 (11)	50 (6)
C(25)	5670 (6)	2626 (3)	-2199 (11)	58 (7)
C(26)	4900 (6)	2617 (3)	-2729 (11)	63 (7)
C(27)	4347 (5)	2907 (3)	-2241 (11)	57 (7)

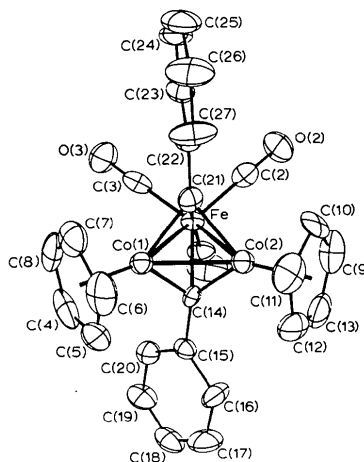


Fig. 1. The atom-numbering scheme.

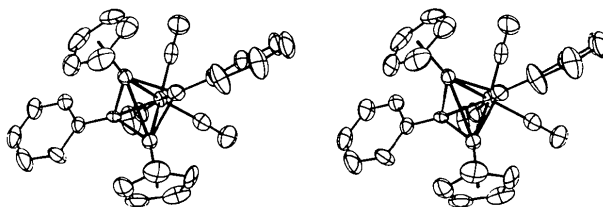


Fig. 2. A stereoview of the molecule, with atoms drawn as 50% probability thermal ellipsoids.

1.880 (7) Å, significantly shorter than the mean distance to the Fe atom, 1.973 (22) Å (4.1σ). The two C(carbyne) atoms are separated by 2.61 (1) Å, slightly more than the value of 2.544 (14) Å in the complex of Fritch *et al.* (1979) and that of 2.546 (9) Å found by Yamazaki *et al.* (1979). The M—C(carbyne)—C(phenyl) angles range from 126.2 (5) to 138.2 (5)° at C(14), and from 131.6 (5) to 133.8 (6)° at C(21); thus the carbyne ligands are bonded almost perpendicularly to the triangular metal plane. The C(carbyne)—C(phenyl) distances are indistinguishable, 1.474 (9) and 1.483 (9) Å, and representative of single bonds to sp^2 -hybridized C atoms in the phenyl rings.

The carbonyl ligands are unexceptional [mean dimensions Fe—C 1.816 (18), C—O 1.12 (1) Å, \angle Fe—C—O, 177 (1)°], though the C—Fe—C angles range from 93.9 (4) to 100.5 (4)°. Distances and angles within the cyclopentadienyl ligands and the phenyl rings have been deposited.* Ring *A*, bonded to Co(1), has a mean Co—C distance of 2.084 (4) Å, and a mean C—C distance of 1.394 (5) Å, while ring *B*, bonded to Co(2), has Co—C distances ranging from 2.070 (8) to 2.120 (9) Å, and a mean C—C distance of 1.418 (5) Å. In each case the normals from Co(1) and Co(2) to the planar ligands *A* and *B* lie almost exactly in the FeCo₂ plane, at 1.0 (5) and 3.5 (3)° respectively. The mean C—C—C angle within the two ligands is 108.0 (4)°. The two phenyl rings on the carbyne ligands are also planar. Distances in ring *C* range from 1.34 (1) to 1.40 (1), in ring *D* from 1.35 (1) to 1.39 (1) Å. Angles range from 117.0 (8) to 121.8 (9)° in ring *C*, and from 117.3 (7) to 122.3 (9)° in ring *D*. Such variations are often observed (Farrar & Payne, 1981).

The disposition of the phenyl-ring substituents upon the C(carbyne) atom is worthy of comment. Dellaca & Penfold (1972) in their analysis of $[\mu_3\eta^1\text{-C}(\text{C}_6\text{H}_5)]\text{-}[\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3\text{Co}][\text{Co}(\text{CO})_3]_2$ showed the plane of the phenyl ring to lie parallel with a Co—Co bond due to *m* site symmetry. In contrast, Holloway (1978) in a study of the complex $[\mu_3\eta^1\text{-C}(\text{C}_6\text{H}_5)]\text{-}[\eta^6\text{-C}_7\text{H}_8][\text{Co}(\text{CO})_2]_3$ found the phenyl substituent to bisect one Co—Co—Co angle. In the present compound a similar arrangement is observed, in that the plane of phenyl-group *C* is almost perpendicular [82.2 (3)°] to the Co—Co bond, while the plane of phenyl-ring *D* makes an angle of 73.4 (3)° with the Co(1)—Fe bond. Since the C(carbyne)—C(phenyl) bond is apparently single (see above), some weak interaction, presumably between the π cloud of the rings and the orbitals of the triangular

cluster, must be responsible for the conformation observed in the solid state. Schilling & Hoffmann (1979) have addressed the problem of the preferred orientation of a ligand bonded through a single atom to a triangular cluster of metal atoms, and concluded that the barrier to rotation will be small if the C(carbyne)—C(phenyl) bond is upright. In the present case non-bonding steric interactions with the *ortho*-H atoms may also be important. Phenyl-ring *D* bisects the C(2)—Fe—C(3) angle, with non-bonded distances from HC(23) to C(2) and C(3) of 2.83 and 2.75 Å respectively. Ring *C* is unable to adopt this orientation due to the presence of C(1)O(1); instead it makes an angle of 73.4 (3)° with the Co(1)—Fe bond, an orientation in which HC(20) is bracketed by C(1) and HC(4), both at 2.76 Å.

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* See deposition footnote.