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Electron transfer in organometallic clusters

XIV *. Crystal and electronic structures of the tricobalt carbon cluster (η^5-C_5H_5)Fe[η^5-C_5H_4-$CCo_3(CO)_9$] and the biscarbyne cluster (η^5-C_5H_5)Fe[η^5-$C_5H_4CCo_3$(η^5-C_5H_5)$_3$CH]

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Abstract

The crystal and molecular structures of (η^5-C_5H_5)Fe[η^5-$C_5H_4CCo_3(CO)_9$] (**1**), $Pna2_1$, a 17.354, b 11.463, c 11.207 Å, $Z = 4$, $R = 0.053$, $R_w = 0.056$ for 939 reflections ($I > 3\sigma(I)$) at 293 K, and (η^5-C_5H_5)Fe[η^5-$C_5H_4CCo_3$(η^5-C_5H_5)$_3$CH] (**2**), $P2_1/n$, a 13.807(9), b 11.254(4), c 13.991(9) Å, β 99.98(5)°, $Z = 4$, $R = 0.033$ and $R_w = 0.033$ for 3051 observed reflections ($I > 3\sigma(I)$) at 180 K, have been determined by X-ray methods.

The results provide a detailed characterisation of related tricobalt-carbon complexes directly bound to ferrocene residues. In **1** the ferrocenyl moiety tops the pyramidal CCo_3 cluster core, while in **2** the CCo_3C core is bipyramidal with a ferrocenyl substituent on one capping carbon atom and a hydrogen atom at the other. In both cases the ferrocenyl group is tilted towards one cobalt atom of the cluster core, a distortion believed to be the consequence of the non-degeneracy of the carbyne $p(\pi)$ orbitals resulting from a cooperative π-interaction between the clusters and the ferrocenyl substituents.

Earlier papers in this series [2–4] have described the preparation and redox chemistry of molecules in which a tricobalt-carbon or bis-carbyne cluster unit is directly linked to a ferrocene moiety through a capping carbon atom. Such molecules have two or three potential redox sites; the ferrocene moiety readily acts as an oxidation centre while both the +1 and −1 oxidation states are accessible to the cluster or its derivatives. An analysis of the electrochemical and spectral data for

* For part XIII see ref. 1.

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these compounds pointed to a weak interaction between the ferrocene and cluster based redox sites and it was suggested that this interaction had both inductive and mesomeric components. The crystal structure analyses of the prototypal compounds $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4CCo_3(CO)_9]$ (**1**) and $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4CCo_3(\eta^5\text{-}C_5H_5)_3CH]$ (**2**) reported here were undertaken to determine the possible structural ramifications of coupling between the ferrocene and tricobalt-carbon moieties.

Experimental

Details of the crystals, data collections and structure refinements are summarised in Table 1.

Compound 1

A sample of **1**, prepared as outlined previously [2], was recrystallised from hexane yielding red prisms. Precession photography (Cu-K_α radiation) indicated an ortho-

Table 1

Crystal data, data collections and refinements of **1** and **2**

	1	**2**
Crystal data		
Crystal system	orthorhombic	monoclinic
Space group	$Pna2_1$	$P2_1/n$
a	17.354(3) Å	13.807(9) Å
b	11.463(2) Å	11.254(4) Å
c	11.207(2) Å	13.991(9) Å
β	–	99.98(5)°
V	2229 Å^3	2141 Å^3
Formula	$C_{20}H_9O_9Co_3Fe$	$C_{27}H_{25}Co_3Fe$
Formula weight	625.9 g mol^{-1}	582.2 g mol^{-1}
D_c	1.86 g cm^{-3}	1.76 g cm^{-3}
D_m	–	1.75(3) g cm^{-3}
Z	4	4
$F(000)$	1232	294
Crystal size	0.4×0.6×0.6 mm^3	0.45×0.3×0.25 mm^3
Mo-K_α	28.5 cm^{-1}	7.40 cm^{-1}
Data collections and refinements		
Diffractometer	Hilger and Watts	Nicolet P$\bar{3}$
Temperature	293(1) K	180(5) K
Radiation	Mo-K_α (λ 0.71069 Å)	Mo-K_α (λ 0.71069 Å)
Scan type	θ–2θ	θ–2θ
Data limits	$0 < 2\theta < 50°$	$1 < 2\theta < 50°$
Reflections measured	$\pm h,k,l$	$\pm h,k,l$
Total observed data	1639	3755
Unique data	939 ($I > 3\sigma(I)$)	3051 ($I > 3\sigma(I)$)
Absorbtion correction	numerical [a]	numerical [b]
Number of variables	154	281
$R(\Sigma\|\|F_o\|-\|F_c\|\|/\|F_o\|)$	0.0529	0.0334
R_w $[\Sigma w^{1/2}\|\|F_o\|-\|F_c\|\|/\Sigma w^{1/2}\|F_o\|]$	0.0561	0.0331
w	$[0.8912/(\sigma^2F+0.003076F^2)]$	$[1.000/\sigma^2F+0.0001F^2)]$

[a] See ref. 6. [b] See ref. 10.

rhombic unit cell and the space group was confirmed as $Pna2_1$ by the success of the structure refinement. The data were processed using the program HILGOUT [5] and analytical absorption corrections applied with the program ABSORB [6].

The structure was solved by direct methods using the program MULTAN [7]. The chosen E-map revealed the location of the cobalt triangle, the Fe atom and several of the C atoms of the cyclopentadiene rings. The remaining non-hydrogen atoms were found in subsequent difference Fourier, least-squares refinement cycles using the program SHELX-76 [8]. Hydrogen atoms on the cyclopentadiene rings were included in calculated positions (d(C–H) 1.08 Å) with fixed isotropic thermal parameters. Refinement, with anisotropic temperature factors for the Co and Fe atoms and a weighting scheme based on counting statistics, converged with final values of R and R_w of 0.0529 and 0.0561 respectively. A final difference Fourier showed no anomalously high peaks (highest peak 0.54 eÅ^{-3}) and the minimised function showed little dependence on $|F_o|$ or $\sin\theta/\lambda$.

Table 2

Final positional and equivalent thermal parameters for **1**

Atom	x	y	z	U_{eq}/U_{11}
Fe(1)	0.5851(2)	0.0388(3)	−0.5786	0.039
Co(1)	0.7172(2)	0.4057(3)	−0.4436(5)	0.044
Co(2)	0.5817(2)	0.4281(3)	−0.5038(4)	0.044
Co(3)	0.6826(2)	0.3961(3)	−0.6572(5)	0.043
C(11)	0.693(2)	0.386(3)	−0.292(3)	0.078(9)
C(12)	0.802(1)	0.319(2)	−0.442(3)	0.052(6)
C(13)	0.755(2)	0.550(3)	−0.442(3)	0.070(8)
C(21)	0.503(2)	0.406(2)	−0.602(3)	0.063(8)
C(22)	0.532(2)	0.391(2)	−0.377(3)	0.057(7)
C(23)	0.582(2)	0.586(3)	−0.491(3)	0.075(8)
C(31)	0.764(2)	0.327(2)	−0.708(3)	0.062(8)
C(32)	0.625(2)	0.354(2)	−0.779(3)	0.060(7)
C(33)	0.698(2)	0.546(3)	−0.704(3)	0.061(8)
O(11)	0.675(1)	0.369(2)	−0.198(2)	0.094(7)
O(12)	0.853(1)	0.253(2)	−0.451(2)	0.078(6)
O(13)	0.780(1)	0.644(2)	−0.447(3)	0.099(7)
O(21)	0.451(1)	0.395(2)	−0.665(2)	0.078(6)
O(22)	0.497(1)	0.365(2)	−0.291(2)	0.081(6)
O(23)	0.586(1)	0.683(2)	−0.481(2)	0.091(7)
O(31)	0.819(1)	0.273(2)	−0.734(2)	0.080(6)
O(32)	0.588(1)	0.324(2)	−0.861(2)	0.089(6)
O(33)	0.718(1)	0.640(2)	−0.723(2)	0.107(8)
C_{ap}(1)	0.650(1)	0.299(2)	−0.533(2)	0.037(6)
C(1)	0.648(1)	0.174(2)	−0.508(2)	0.030(5)
C(2)	0.696(1)	0.088(2)	−0.558(2)	0.036(5)
C(3)	0.682(1)	−0.025(2)	−0.501(2)	0.042(5)
C(4)	0.628(2)	−0.006(2)	−0.415(2)	0.051(7)
C(5)	0.604(1)	0.119(2)	−0.418(2)	0.040(6)
C(6)	0.504(2)	0.094(3)	−0.699(3)	0.08(1)
C(7)	0.559(2)	0.019(3)	−0.757(3)	0.08(1)
C(8)	0.552(2)	−0.091(3)	−0.702(3)	0.09(1)
C(9)	0.497(2)	−0.078(3)	−0.610(3)	0.068(8)
C(10)	0.467(2)	0.035(3)	−0.607(3)	0.079(9)

Compound 2

Crystals of **2** [4] were grown from hexane, and a black rhomb used for data collection. Oscillation and Weissenberg photography (Cu-K_α radiation) showed a monoclinic crystal with the systematic absences ($h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$) consistent with the space group $P2_1/n$. Intensity data was collected at 180 K.

The positions of the three Co atoms and the Fe atom, found in an ambient temperature determination of **2** [9], were used to phase the initial structure factor calculation. Difference syntheses and least-squares refinements were performed using the program SHELXTL [10] to locate the remaining non-hydrogen atoms. The positions of the cyclopentadienyl and apical hydrogen atoms were calculated (d(C–H) 0.96 Å) and a common isotropic temperature factor refined. All non-hydrogen atoms were refined anisotropically and a weighting scheme introduced in the final stages of the refinement. Convergence with this model was reached with $R = 0.0334$, $R_w = 0.0331$. The largest residual peak in a final difference Fourier map appeared with a height of 0.56 eÅ^{-3} and the weighting scheme appeared satisfactory.

(continued on p. 421)

Table 3

Final positional and equivalent thermal parameters for **2**

Atom	x	y	z	U_{eq}
Fe	0.2192(1)	0.0864(1)	0.5852(1)	0.022
Co(1)	0.2174(1)	0.4861(1)	0.4308(1)	0.017
Co(2)	0.1510(1)	0.3343(1)	0.3210(1)	0.018
Co(3)	0.3228(1)	0.3443(1)	0.3743(1)	0.017
C_{ap}(1)	0.2238(2)	0.3204(3)	0.4476(3)	0.017
C_{ap}(2)	0.2387(3)	0.4538(3)	0.3055(3)	0.020
C(11)	0.2072(3)	0.6725(3)	0.4371(3)	0.028
C(12)	0.1196(3)	0.6179(4)	0.4479(3)	0.031
C(13)	0.1364(3)	0.5455(4)	0.5322(3)	0.039
C(14)	0.2366(4)	0.5530(4)	0.5734(3)	0.039
C(15)	0.2788(3)	0.6307(4)	0.5135(3)	0.031
C(21)	0.0728(3)	0.3209(4)	0.1782(3)	0.034
C(22)	0.0154(3)	0.3728(4)	0.2408(3)	0.034
C(23)	0.0059(3)	0.2911(4)	0.3158(3)	0.031
C(24)	0.0579(3)	0.1834(4)	0.2994(3)	0.029
C(25)	0.1000(3)	0.2066(4)	0.2148(3)	0.033
C(31)	0.4633(3)	0.3954(4)	0.3640(3)	0.027
C(32)	0.4627(3)	0.3314(4)	0.4522(3)	0.027
C(33)	0.4279(3)	0.2158(4)	0.4269(3)	0.028
C(34)	0.4049(3)	0.2101(4)	0.3231(3)	0.029
C(35)	0.4273(3)	0.3212(4)	0.2852(3)	0.027
C(1)	0.2146(3)	0.2616(3)	0.5388(3)	0.017
C(2)	0.2925(3)	0.2418(4)	0.6208(3)	0.022
C(3)	0.2514(3)	0.1999(4)	0.7013(3)	0.026
C(4)	0.1494(3)	0.1907(4)	0.6718(3)	0.029
C(5)	0.1270(3)	0.2270(4)	0.5717(3)	0.024
C(6)	0.2364(4)	−0.0209(4)	0.4706(3)	0.038
C(7)	0.3148(4)	−0.0369(4)	0.5495(3)	0.038
C(8)	0.2762(3)	−0.0756(4)	0.6315(3)	0.037
C(9)	0.1746(4)	−0.0838(4)	0.6042(3)	0.040
C(10)	0.01492(4)	−0.0493(4)	0.5057(3)	0.039

Table 4

Selected bond lengths (Å) and angles (°) for **1** and **2**

Molecule **1**		Molecule **2**	
Fe–C(1)	2.05(2)	Fe–C(1)	2.071(4)
Fe–C(2)	2.02(2)	Fe–C(2)	2.045(5)
Fe–C(3)	2.04(2)	Fe–C(3)	2.039(4)
Fe–C(4)	2.04(3)	Fe–C(4)	2.042(5)
Fe–C(5)	2.04(2)	Fe–C(5)	2.030(4)
Fe–C(6)	2.05(3)	Fe–C(6)	2.037(5)
Fe–C(7)	2.06(3)	Fe–C(7)	2.046(5)
Fe–C(8)	2.11(3)	Fe–C(8)	2.047(5)
Fe–C(9)	2.06(3)	Fe–C(9)	2.045(5)
Fe–C(10)	2.07(3)	Fe–C(10)	2.031(5)
Co(1)–Co(2)	2.460(5)	Co(1)–Co(2)	2.365(2)
Co(1)–Co(3)	2.470(5)	Co(1)–Co(3)	2.394(2)
Co(2)–Co(3)	2.481(5)	Co(2)–Co(3)	2.391(2)
Co(1)–C_{ap}(1)	1.97(2)	Co(1)–C_{ap}(1)	1.880(4)
Co(2)–C_{ap}(1)	1.93(2)	Co(2)–C_{ap}(1)	1.870(3)
Co(3)–C_{ap}(1)	1.87(2)	Co(3)–C_{ap}(1)	1.871(4)
		Co(1)–C_{ap}(2)	1.842(4)
		Co(2)–C_{ap}(2)	1.858(4)
		Co(3)–C_{ap}(2)	1.849(4)
C_{ap}(1)–C(1)	1.45(3)	C_{ap}(1)–C(1)	1.448(5)
C(1)–C(2)	1.40(3)	C(1)–C(2)	1.447(5)
C(1)–C(5)	1.41(3)	C(1)–C(5)	1.433(6)
C(2)–C(3)	1.47(3)	C(2)–C(3)	1.418(6)
C(3)–C(4)	1.37(3)	C(3)–C(4)	1.419(6)
C(4)–C(5)	1.48(3)	C(4)–C(5)	1.423(5)
C(6)–C(7)	1.43(4)	C(6)–C(7)	1.418(6)
C(6)–C(10)	1.40(4)	C(6)–C(10)	1.425(7)
C(7)–C(8)	1.41(4)	C(7)–C(8)	1.406(7)
C(8)–C(9)	1.40(4)	C(8)–C(9)	1.408(7)
C(9)–C(10)	1.39(4)	C(9)–C(10)	1.400(6)
Co(1)–C(11)	1.77(4)	Co(1)–C(11)	2.105(4)
C(11)–O(11)	1.12(4)	Co(1)–C(12)	2.059(5)
Co(1)–C(12)	1.78(2)	Co(1)–C(13)	2.060(5)
C(12)–O(12)	1.16(3)	Co(1)–C(14)	2.081(4)
Co(1)–C(13)	1.78(3)	Co(1)–C(15)	2.086(4)
C(13)–O(13)	1.16(3)	C(11)–C(12)	1.402(6)
Co(2)–C(21)	1.77(3)	C(11)–C(15)	1.405(6)
C(21)–O(21)	1.15(3)	C(12)–C(13)	1.407(6)
Co(2)–C(22)	1.72(3)	C(13)–C(14)	1.421(7)
C(22)–O(22)	1.18(3)	C(14)–C(15)	1.402(7)
Co(2)–C(23)	1.82(3)	Co(2)–C(21)	2.088(4)
C(23)–O(23)	1.12(3)	Co(2)–C(22)	2.071(4)
Co(3)–C(31)	1.71(3)	Co(2)–C(23)	2.076(4)
C(31)–O(31)	1.18(3)	Co(2)–C(24)	2.084(4)
Co(3)–C(32)	1.76(3)	Co(2)–C(25)	2.089(5)
C(32)–O(32)	1.17(3)	C(21)–C(22)	1.405(6)
Co(3)–C(33)	1.82(3)	C(21)–C(25)	1.410(7)
C(33)–O(33)	1.15(3)	C(22)–C(23)	1.408(6)
		C(23)–C(24)	1.405(6)
		C(24)–C(25)	1.411(6)
		Co(3)–C(31)	2.077(4)
		Co(3)–C(32)	2.070(4)
		Co(3)–C(33)	2.093(4)

(continued)

Table 4 (continued)

Molecule 1		Molecule 2	
		Co(3)–C(34)	2.094(5)
		Co(3)–C(35)	2.083(4)
		C(31)–C(32)	1.416(6)
		C(31)–C(35)	1.394(6)
		C(32)–C(33)	1.401(6)
		C(33)–C(34)	1.416(6)
		C(34)–C(35)	1.412(6)
Co(2)–Co(1)–Co(3)	60.4(1)	Co(2)–Co(1)–Co(3)	60.3(1)
Co(2)–Co(1)–C_{ap}(1)	50.1(6)	Co(2)–Co(1)–C_{ap}(1)	50.7(1)
Co(3)–Co(1)–C_{ap}(1)	48.2(6)	Co(3)–Co(1)–C_{ap}(1)	50.2(1)
		Co(2)–Co(1)–C_{ap}(2)	50.6(1)
		Co(3)–Co(1)–C_{ap}(2)	49.7(1)
		C_{ap}(1)–Co(1)–C_{ap}(2)	84.7(2)
Co(1)–Co(2)–Co(3)	60.0(1)	Co(1)–Co(2)–Co(3)	60.4(1)
Co(1)–Co(2)–C_{ap}(1)	51.7(6)	Co(1)–Co(2)–C_{ap}(1)	51.1(1)
Co(3)–Co(2)–C_{ap}(1)	48.2(6)	Co(3)–Co(2)–C_{ap}(1)	50.3(1)
		Co(1)–Co(2)–C_{ap}(2)	50.0(1)
		Co(3)–Co(2)–C_{ap}(2)	49.7(1)
		C_{ap}(1)–Co(2)–C_{ap}(2)	84.6(2)
Co(1)–Co(3)–Co(2)	59.6(1)	Co(1)–Co(3)–Co(2)	59.2(1)
Co(1)–Co(3)–C_{ap}(1)	51.8(6)	Co(1)–Co(3)–C_{ap}(1)	50.5(1)
Co(2)–Co(3)–C_{ap}(1)	50.2(6)	Co(2)–Co(30–C_{ap}(1)	50.3(1)
		Co(1)–Co(3)–C_{ap}(2)	49.4(1)
		Co(2)–Co(3)–C_{ap}(2)	50.0(1)
		C_{ap}(1)–Co(3)–C_{ap}(2)	84.8(2)
Co(1)–C_{ap}(1)–Co(2)	78.3(8)	Co(1)–C_{ap}(1)–Co(2)	78.2(1)
Co(1)–C_{ap}(1)–Co(3)	80.0(8)	Co(1)–C_{ap}(1)–Co(3)	79.3(2)
Co(2)–C_{ap}(1)–Co(3)	81.6(8)	Co(2)–C_{ap}(1)–Co(3)	79.4(1)
Co(1)–C_{ap}(1)–C(1)	121(2)	Co(1)–C_{ap}(1)–C(1)	123.4(3)
Co(2)–C_{ap}(1)–C(1)	135(2)	Co(2)–C_{ap}(1)–C(1)	137.3(3)
Co(3)–C_{ap}(1)–C(1)	137(2)	Co(3)–C_{ap}(1)–C(1)	136.2(3)
		Co(1)–C_{ap}(2)–Co(2)	79.4(2)
		Co(1)–C_{ap}(2)–Co(3)	80.9(1)
		Co(2)–C_{ap}(2)–Co(3)	80.3(1)
C_{ap}(1)–C(1)–C(2)	126(2)	C_{ap}(1)–C(1)–C(2)	125.6(3)
C_{ap}(1)–C(1)–C(5)	126(2)	C_{ap}(1)–C(1)–C(5)	127.6(3)
C(2)–C(1)–C(5)	106(2)	C(2)–C(1)–C(5)	106.2(3)
C(1)–C(2)–C(3)	110(2)	C(1)–C(2)–C(3)	108.1(3)
C(2)–C(3)–C(4)	105(2)	C(2)–C(3)–C(4)	109.0(3)
C(3)–C(4)–C(5)	109(2)	C(3)–C(4)–C(5)	107.3(4)
C(1)–C(5)–C(4)	107(2)	C(1)–C(5)–C(4)	109.3(3)
C(7)–C(6)–C(10)	110(3)	C(7)–C(6)–C(10)	107.7(4)
C(6)–C(7)–C(8)	106(3)	C(6)–C(7)–C(8)	107.7(4)
C(7)–C(8)–C(9)	106(3)	C(7)–C(8)–C(9)	108.4(4)
C(8)–C(9)–C(10)	111(3)	C(8)–C(9)–C(10)	108.5(4)
C(6)–C(10)–C(9)	104(3)	C(6)–C(10)–C(9)	107.7(4)
C(11)–Co(1)–C_{ap}(1)	105(1)	C_{ap}(1)–Co(1)–C(11)	170.3(2)
C(12)–Co(1)–C_{ap}(1)	98(1)	C_{ap}(1)–Co(1)–C(12)	136.0(2)
C(13)–Co(1)–C_{ap}(1)	143(1)	C_{ap}(1)–Co(1)–C(13)	105.0(2)
C(21)–Co(2)–C_{ap}(1)	104(1)	C_{ap}(1)–Co(1)–C(14)	104.3(2)
C(22)–Co(2)–C_{ap}(1)	105(1)	C_{ap}(1)–Co(1)–C(15)	134.4(2)
C(23)–Co(2)–C_{ap}(1)	141(1)	C_{ap}(2)–Co(1)–C(11)	105.0(2)
C(31)–Co(3)–C_{ap}(1)	102(1)	C_{ap}(2)–Co(1)–C(12)	118.0(2)
C(32)–Co(3)–C_{ap}(1)	104(1)	C_{ap}(2)–Co(1)–C(13)	154.2(2)
C(33)–Co(3)–C_{ap}(1)	145(1)	C_{ap}(2)–Co(1)–C(14)	160.8(2)

Table 4 (continued)

Molecule 1		Molecule 2	
Co(2)–Co(1)–C(11)	92(1)	C_{ap}(2)–Co(1)–C(15)	123.3(2)
Co(2)–Co(1)–C(12)	148.4(8)	C(12)–C(11)–C(15)	107.3(4)
Co(2)–Co(1)–C(13)	105.0(9)	C(11)–C(12)–C(13)	108.5(4)
Co(3)–Co(1)–C(11)	150(1)	C(12)–C(13)–C(14)	108.0(4)
Co(3)–Co(1)–C(12)	100(1)	C(13)–C(14)–C(15)	106.8(4)
Co(3)–Co(1)–C(13)	98(1)	C(11)–C(15)–C(14)	109.4(4)
Co(1)–C(11)–O(11)	176(3)	C_{ap}(1)–Co(2)–C(21)	171.0(2)
Co(1)–C(12)–O(12)	171(2)	C_{ap}(1)–Co(2)–C(22)	144.8(2)
Co(1)–C(13)–O(13)	176(3)	C_{ap}(1)–Co(2)–C(23)	112.6(2)
Co(1)–Co(2)–C(21)	153.2(9)	C_{ap}(1)–Co(2)–C(24)	107.1(2)
Co(1)–Co(2)–C(22)	103.1(9)	C_{ap}(1)–Co(2)–C(25)	131.5(2)
Co(1)–Co(2)–C(23)	94(1)	C_{ap}(2)–Co(2)–C(21)	101.0(2)
Co(3)–Co(2)–C(21)	95.4(9)	C_{ap}(2)–Co(2)–C(22)	110.4(2)
Co(3)–Co(2)–C(22)	153.1(9)	C_{ap}(2)–Co(2)–C(23)	145.7(2)
Co(3)–Co(2)–C(23)	101(1)	C_{ap}(2)–Co(2)–C(24)	164.2(2)
Co(2)–C(21)–O(21)	177(2)	C_{ap}(2)–Co(2)–C(25)	124.7(2)
Co(2)–C(22)–O(22)	178(3)	C(22)–C(21)–C(25)	107.9(4)
Co(2)–C(23)–O(23)	177(3)	C(21)–C(22)–C(23)	108.5(4)
Co(1)–Co(3)–C(31)	98(1)	C(22)–C(23)–C(24)	107.6(4)
Co(1)–Co(3)–C(32)	154.6(9)	C(23)–C(24)–C(25)	108.4(4)
Co(1)–Co(3)–C(33)	101.4(9)	C(21)–C(25)–C(24)	107.6(4)
Co(2)–Co(3)–C(31)	151(1)	C_{ap}(1)–Co(3)–C(31)	151.0(2)
Co(2)–Co(3)–C(32)	100.3(9)	C_{ap}(1)–Co(3)–C(32)	115.5(2)
Co(2)–Co(3)–C(33)	99.5(9)	C_{ap}(1)–Co(3)–C(33)	104.7(2)
Co(3)–C(31)–O(31)	174(3)	C_{ap}(1)–Co(3)–C(34)	125.4(2)
Co(3)–C(32)–O(32)	178(3)	C_{ap}(1)–Co(3)–C(35)	164.2(2)
Co(3)–C(33)–O(33)	169(3)	C_{ap}(2)–Co(3)–C(31)	107.9(2)
		C_{ap}(2)–Co(3)–C(32)	140.8(2)
		C_{ap}(2)–Co(3)–C(33)	169.1(2)
		C_{ap}(2)–Co(3)–C(34)	130.2(2)
		C_{ap}(2)–Co(3)–C(35)	103.3(2)
		C(32)–C(31)–C(35)	108.1(4)
		C(31)–C(32)–C(33)	107.9(3)
		C(32)–C(33)–C(34)	108.0(4)
		C(33)–C(34)–C(35)	107.5(4)
		C(31)–C(35)–C(34)	108.4(4)

Final positional and equivalent thermal parameters for **1** and **2** are listed in Tables 2 and 3 respectively. A comparative listing of selected bond distances and angles for both molecules appears in Table 4 using the numbering scheme detailed in Figs. 1 and 2. Tables of thermal parameters, H-atom parameters, structure factors and meanplane data can be obtained from the authors (J.S.).

Results and discussion

Structures of 1 and 2

Both compounds consist of well separated monomeric molecules in the crystalline state. No unusual intermolecular contacts are found in either structure, the closest (not involving H atoms) being 3.08 Å between O(21) and O(31) for **1** and 3.41 Å

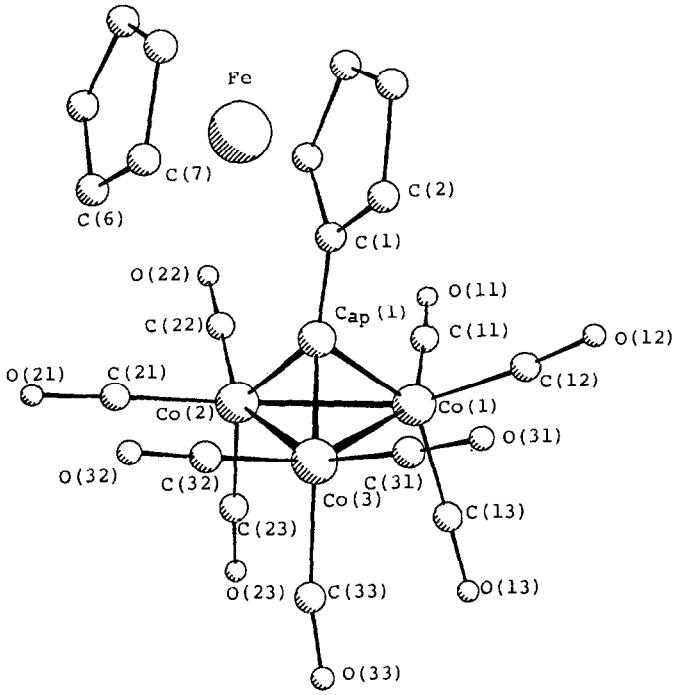


Fig. 1. Structure of **1** showing the atom-numbering scheme. For clarity H atoms have been omitted and only the first two atoms of the consecutively numbered cyclopentadienyl rings have been labelled.

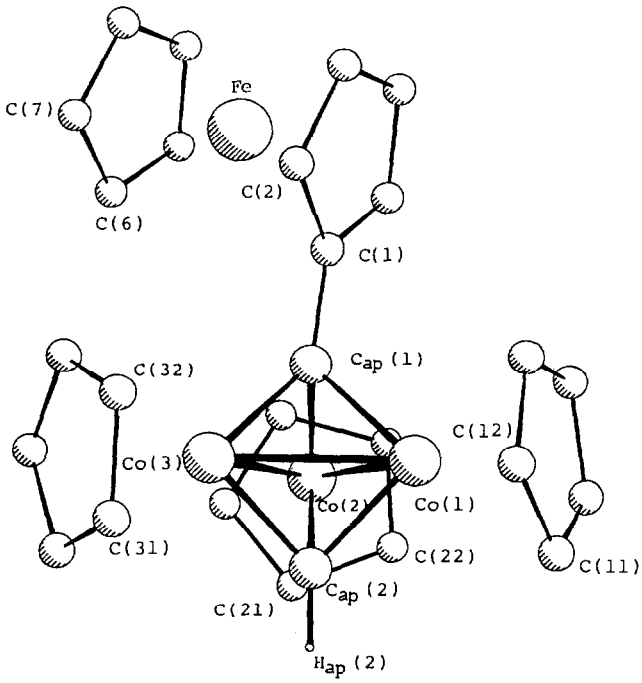


Fig. 2. Structure of **2** showing the atom-numbering scheme. For clarity H atoms have been omitted and only the first two atoms of the consecutively numbered cyclopentadienyl rings have been labelled.

between C(10) and C(11) for **2**. It appears unlikely therefore that crystal packing effects would influence the geometry of either molecule in the solid state.

The structure of **1** (Fig. 1) is based on a pyramidal CCo_3 unit topped by a ferrocenyl residue in which the two cyclopentadienyl rings adopt an eclipsed configuration. The two molecular components are linked through the apical carbon atom atom, C_{ap}, of the cluster unit and the carbon atom C(1) of the ferrocene moiety. The molecule conforms to approximately *Cs-m* geometry, with the pseudo mirror plane bisecting the Co_3 triangle, both cyclopentadienyl rings and passing through the linking C_{ap}–C(1) bond and the Fe atom. Molecule **2** is based on a bipyramidal CCo_3C unit with a hydrogen atom bound to one μ_3-carbon atom and a ferrocenyl moiety, in a similar conformation to that found in **1**, at the other. The cluster and ferrocene units are linked through the $C_{ap}(1)$–C(1) bond. This molecule too approximates to Cs-*m* symmetry with a pseudo mirror plane bisecting both the cluster and ferrocenyl units.

Molecule **1** has a pyramidal cluster core comprising 3 Co atoms capped by the carbyne atom of the μ_3-Fc-carbyne ligand. The basal Co_3 triangle is essentially symmetrical with normal Co–Co distances (mean 2.470(8) Å) and the Co–C_{ap} bond lengths do not deviate significantly from the norm [11], mean Co–C_{ap} 1.92(4) Å. Each Co atom carries the anticipated two equatorial and one axial carbonyl substituents. The Co–(carbonyl C) and C–O distances are unremarkable. Some evidence for the necessity to minimise intermolecular contacts between the carbonyl ligands and the C(1) – – – C(5) ring of the ferrocene moiety is found in the observation that the equatorial carbonyl substituents on Co(2) and Co(3) are bent back slightly towards the Co_3 plane. Dihedral angles of 25 and 26° are found between the Co(1)–Co(2)–Co(3) plane and the planes containing C(21)–Co(2)–C(22) and C(31)–Co(3)–C(32) respectively. These compare with an angle of 32° between the Co_3 plane and the C(11)–Co(1)–C(12) plane where possible interaction between the CO ligands and the Fc substituent is minimised. In tricobalt carbon systems where the steric requirements of the apical substituents are not excessive, the average dihedral angle involving these planes is found to be 30° [11].

The bipyramidal CCo_3C core of **2** consists of a triangle of cobalt atoms capped on opposite sides by two μ_3-bonded carbyne ligands, derived from alkyne cleavage of the acetylene precursor FcC≡CH [4]. The Co_3 triangle is distorted slightly with two long and one short Co–Co bonds while the Co–$C_{ap}(1)$ bonds show no significant variation (mean 1.874(4) Å) and are in the range normally found in tricobalt biscarbyne complexes [13–15]. All Co–$C_{ap}(2)$ bonds are also equivalent (mean 1.850(6) Å), but are significantly shorter than those to $C_{ap}(1)$ or those previously reported for analogous systems. This shortening may reflect the additional electron density available to the cluster core resulting from electron release by the Fc substituent (vide infra). Each Co atom carries an η^5-Cp ring and the mean Co–C(ring) distance, 2.08(1) Å, agrees well with values previously observed in mono- [12] and bicapped [13,14] cobalt clusters with η^5-Cp ligands. The orientation of these Cp rings with respect to the Co_3 plane is such that the dihedral angles are 87°, C(11) – – – C(15), 87°, C(21) – – – C(25), and 88°, C(31) – – – C(35). Hence each cobalt bound Cp ring is bent slightly away from an orientation normal to the Co_3 triangle and away from the ferrocenyl substituent. It is notable however that the bending is essentially equivalent for all three rings regardless of their placement with respect to the apical Fc. The distance between the capping carbyne atoms $C_{ap}(1) \cdots C_{ap}(2)$ of the cluster unit is 2.51 Å.

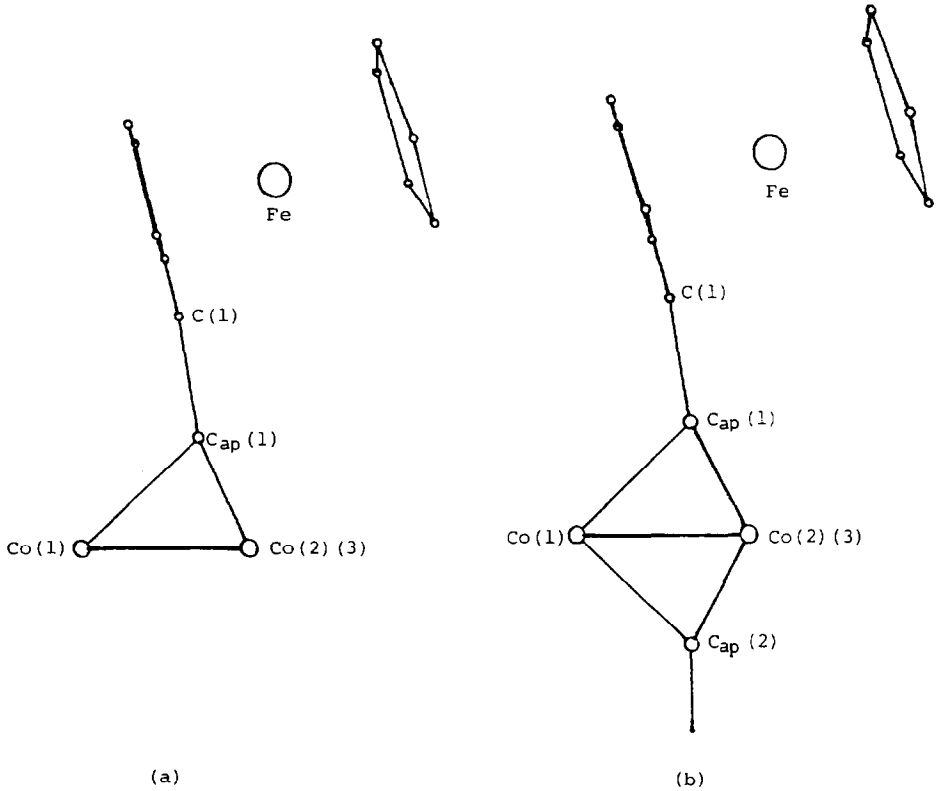


Fig. 3. Structures of (a) **1** and (b) **2** showing the tilt of the Fc substituents.

The most unusual feature of both structures is the orientation of the Fc moiety with respect to the cluster units. In both molecules the $C_{ap}(1)$–C(1) bond is bent away from the threefold axis such that the angle between the C(1)–$C_{ap}(1)$ vector and the centroid of the cobalt triangle is 168° for **1** and 170° for **2**. Further the Fc moieties, which lie over the Co(2)–Co(3) bonds in both molecules, are tilted back further towards Co(1) in that the angle C_{ap}–C(1)–(centroid of the C(1) – – – C(5) ring) is 174° for **1** and 173° for **2**. The deviations are also reflected by a widening of the C(1)–$C_{ap}(1)$–Co(2) and C(1)–$C_{ap}(1)$–Co(3) angles in comparison to the C(1)–$C_{ap}(1)$–Co(1) angles for both molecules. The strikingly similar orientations of the ferrocenyl carbyne ligands in both structures are displayed in Fig. 3.

The positioning of a substituent atom directly bound to the apical carbon atom of tricobalt carbon clusters $YCCo_3$ such that the Y–C bond is perpendicular to the plane of the cobalt triangle is a general feature of these cluster systems [11]. Exceptions occur in molecules where equatorial carbonyl groups are substituted by sterically demanding phosphine ligands and the apical substituent bends away from the bulky phosphine, reducing their non-bonded contact [16,17]. Symmetrical placement is also the norm in known bis-carbyne tricobalt derivatives [13–15] and indeed the H_{ap}–$C_{ap}(2)$ fragment is symmetrically coordinated to the cobalt triangle in molecule **2**.

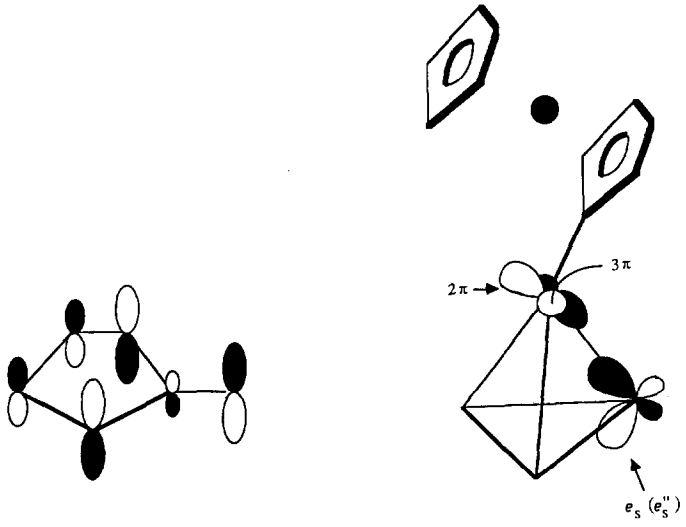
Tricobalt carbon clusters are known [11] to be sterically congested because of close intramolecular contacts between the equatorial carbonyls groups on adjacent

cobalt atoms and between these ligands and the capping carbon atom. It is reasonable therefore to speculate that the tilt of the Fc moiety in **1** tends to reduce non-bonded contacts. However in the bis-carbyne complex, **2**, the cobalt bound η^5-Cp ligands are well separated with no intramolecular ligand–ligand contacts < 3.6 Å. Non-bonded contacts between the η^5-Cp rings of the cluster and their Fc counterparts are all > 3.3 Å, the closest intramolecular contact between the Fc and cluster fragments being 2.94 Å (between C(1) · · · Co(1)) which reflects the tilting of the Fc residue towards Co(1). Furthermore, the splaying of the cobalt bound η^5-Cp ligands away from the normal to the Co_3 triangle is small (~ 2–3°) and approximately equivalent at all three Co atoms. It would appear therefore that for **2**, the minimisation of intramolecular contacts between Fc and the η^5-Cp ligands has little influence on the ultimate orientation of the Fc substituent. The observed tilting actually increases the closest intramolecular contact with the cluster core (particularly Co(1) · · · C(1)). Consequently we conclude that the tilt of the Fc moiety must result from electronic rather than steric interactions in **2** and, a fortiori, contributes significantly to the closely corresponding distortion in **1**.

In common with many ferrocenyl compounds [18] the η^5-Cp ligands in both **1** and **2** adopt an eclipsed configuration. The rings are coplanar within experimental error and the Fe atoms are symmetrically placed with respect to the ring planes. The dihedral angle between the ring planes is 3.6° for **1** and 1.9° for **2**. Both Fe bound η^5-Cp rings in both molecules show apparent deviations in C–C bond lengths but these can not be considered to be significant. Mean values of C–C bond lengths for the C(1) – – – C(5) rings are 1.43(4) Å for **1** and 1.43(1) Å for **2** with corresponding values for the C(6) – – – C(10) rings of 1.41(1) and 1.411(8) Å respectively, results that are not inconsistent with a degree of mesomeric electron release to the cluster unit via the C(1)–C_{ap}(1) bond.

Electronic structures of molecules 1 and 2

Electrochemical and spectroscopic data for **1** and **2** clearly point to a degree of electron delocalisation between the cluster and Fc moieties through the carbyne C atoms of the cluster units [3,4]. The unusual tilt of the Fc–C_{ap}(1) bonds in **1** and **2** can be shown to provide further evidence for such delocalisation as the absence of significant intramolecular contacts between the Fc-C carbyne and the η^5-Cp ligands in **2** (vide supra) negates a steric explanation of the relative orientations of the Fc and cluster redox centres. Furthermore the close similarity of the Fc/cluster orientations in both **1** and **2** points to a common causation. We therefore suggest that the distortions found in these molecules have their origins in an electronic interaction between the Fc and cluster centres, a proposition that takes cognizance of the flexible bonding abilities of a carbyne bound to a cobalt triangle. There is ample evidence for the ability of the CCo_3 unit in tricobalt carbon clusters to engage in "push-pull" electronic interactions with its apical substituents [11]. For example the C_{ap}–halogen bond stretching frequencies of the clusters and their derivatives are anomalously high [19–21] while ^{59}Co and ^{35}Cl NQR spectroscopy provides additional evidence of the π-acceptor ability of the $CCo_3(CO)_9$ moiety [22]. The results of photoelectron studies [23] and molecular orbital calculations [24] on several $YCCo_3(CO)_9$ compounds further attest the ability of the CCo_3 unit to act as a π-acceptor, despite the finding that the apical C atom is electron rich [23]. The chemistry of the related bis(carbyne) systems is not so fully documented, due



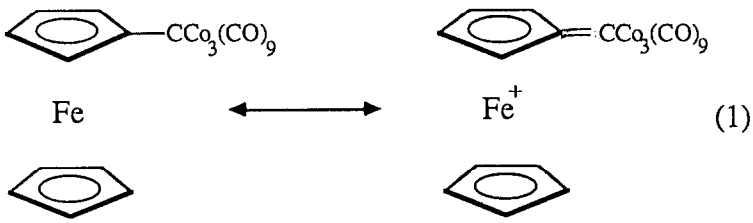
(a) (b)

Fig. 4. (a) The $2\pi_s$ orbital of fulvene. (b) Interaction of the fulvene $2\pi_s$ orbital with the e_s (**1**) or e''_s (**2**) orbitals of the Co_3 triangles.

principally to the difficulties associated with synthesis of the acetylene precursors. There are however no obvious reasons why they should not behave similarly and the bis(carbyne) derivatives have the singular added advantage that, with suitable carbyne capping functions, interaction through the cluster core is possible [4].

The physical data on **1** and **2** strongly suggest that the Fc moiety acts as a π-donor to the Co_3 unit. In order to provide a compatible explanation of the observed structural distortions, a model was chosen which incorporates the carbyne C atom of the cluster core with the substituted η^5-Cp ring to provide a fulvene-like bridge between the Fc and cluster fragments. This approach is similar to that taken by Schilling and Hoffman in their discussion of the cluster carbonium ion $H_2C^+CCo_3(CO)_9$ [24]. The MOs of fulvene are well known [25]. Interaction of the three bonding MOs with the Fe orbitals results in a bonding scheme similar to that derived for ferrocene itself [26]. Fulvene has an additional orbital, $2\pi_s$, Fig. 4(a), which is antibonding in the free ligand but gives a stabilised bonding combination on interaction with the d_{z^2} orbital of the Fe atom. The resultant filled π-combination has considerable electron density at the *exo*-carbon atom ($C_{ap}(1)$ in **1** and **2**) and overlap between the $2\pi_s$ (fulvene) and the symmetrical component, e_s or e''_s, of the $e(\pi)$ MOs of either the $Co_3(CO)_9$ [23,24] and $Co_3(\eta^5\text{-Cp})_3CH$ [4] fragments should stabilise this level still further in a hyperconjugative interaction. On the other hand, the carbyne π-orbital lying in the plane of the C(1) – – – C(5) ring (3π) remains essentially a $p\pi$ orbital of the carbyne C atom. This is a classic example of removal of the degeneracy of the carbyne π-orbitals [27,28] and exemplifies the statement [27] that "non-equivalence of the two empty π-levels in carbynes makes them unique among the π-accepting ligands in their ability to form two non-equivalent π-bonds even with metal fragments whose symmetries are high enough to permit equivalent π-donating orbitals on the metal(s)". The overlap between the

symmetrical components e_s or e''_s and the $2\pi_s$ (fulvene) will increase as the ferrocene moiety tilts towards Co(1) (Fig. 4(b)). Thus the tilt observed in **1** or **2** allows for maximisation of the orbital overlap without greatly increasing the intramolecular contacts and the overall effect is an appreciable hyperconjugative interaction between the Fe atoms and the Co_3 triangles as indicated by the resonance structures (eq. 1).



(1)

The X-ray/PES data of Jolly et al. [29] point to similar strong π-donor interactions when the $CCo_3(CO)_9$ unit carries methoxy or dimethylamido substituents which would also serve to remove the degeneracy of the carbyne π-orbitals [27]. The second carbyne fragment in **2**, $C_{ap}(2)$–$H_{ap}(2)$, cannot be involved in an asymmetric π-interaction and has been ignored in our bonding discussion. The molecular structure of the bis(carbyne) with two equivalent capping FcC fragments [4] would be most interesting in this context [30].

With apical substituents such as Fc, orbital energies and symmetries offer scope for structurally significant π-interactions. This may not be so for less favourable π-donor substituents like Ph and the energy differences between undistorted and energy minimised structures will be small and intra- or intermolecular contacts may be equally important. Indeed the generic $PhCCo_3(CO)_9$ shows no significant tilting of the apical substituent or of the C_{ap}–ring bond [31]. Work is currently in progress in these laboratories to examine other carbyne cluster systems in which stereochemically significant deformations result from a removal of degeneracy of the carbyne π-orbitals.

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References

1 S.D. Jensen, B.H. Robinson and J. Simpson, Organometallics, submitted for publication.
2 S.B. Colbran, B.H. Robinson and J. Simpson, Organometallics, 2 (1983) 943.
3 S.B. Colbran, B.H. Robinson and J. Simpson, Organometallics, 2 (1983) 952.
4 S.B. Colbran, B.H. Robinson and J. Simpson, Organometallics, 3 (1984) 1344.
5 The data processing program HILGOUT is based on the programs DRED (J.F. Blount) and PICKOUT (R.J. Doedens).
6 Program ABSORB, a major modification of AGNOST (L. Templeton and D. Templeton).
7 P. Main, M.M. Woolfson, and G. Germain, MULTAN-78 suite of programs.
8 G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, Cambridge, England, 1975.

9 S.B. Colbran, Ph.D. Thesis, University of Otago, 1983.
10 G.M. Sheldrick, SHELXTL. An integrated system for solving, refining and displaying crystal structures from diffraction data, University of Göttingen, 1980.
11 B.R. Penfold, and B.H. Robinson, Acc. Chem. Res., 6 (1973) 73.
12 R.S. McCallum, and B.R. Penfold, Acta Crystallogr., B24 (1978) 1688.
13 J.R. Fritch, K.P.C. Vollhardt, M.R. Thompson and V.W. Day, J. Am. Chem. Soc., 101 (1979) 2770.
14 H. Yamazaki, Y. Wakatsuki and K. Aoki, Chem. Lett., (1979) 1041.
15 R.B.A. Pardy, G.W. Smith and M.E. Vickers, J. Organomet. Chem., 252 (1983) 341.
16 M.D. Brice, B.R. Penfold, W.T. Robinson and S.R. Taylor, Inorg. Chem., 9 (1970) 362.
17 A.J. Downard, B.H. Robinson and J. Simpson, Organometallics, 5 (1986) 1122.
18 M.R. Churchill and J. Wormald, Inorg Chem., 8 (1969) 716 and references therein.
19 W.T. Dent, L.A. Duncanson, R.E. Guy, H.W.B. Reed and B.L. Shaw, Proc. Chem. Soc. London, (1961) 169.
20 T.W. Matheson, B.H. Robinson and W.S. Tham, J. Chem. Soc., (A) (1971) 1457.
21 P.A. Dawson, B.H. Robinson and J. Simpson, J. Chem. Soc., Dalton Trans., (1979) 1762.
22 D.C. Miller and T.B. Brill, Inorg. Chem., 17 (1978) 240.
23 P.T. Chesky and M.B. Hall, Inorg. Chem., 20 (1981) 4419.
24 B.E.R. Schilling and R. Hoffman, J. Am. Chem. Soc., 101 (1979) 3456.
25 F.A. Cotton, Chemical Applications of Group Theory, (1971) Wiley, New York (Second Edition).
26 E. Heilbronner and H. Bock, The HMO-Model and its Applications. 3. Tables of Huckel Molecular Orbitals, Wiley-Interscience, New York, 1976.
27 N.M. Kostic and R.F. Fenske, J. Am. Chem. Soc., 103 (1981) 4677.
28 N.M. Kostic and R.F. Fenske, J. Am. Chem. Soc., 104 (1982) 3879.
29 S.F. Xiang, A.A. Bakke, H.-W. Chen, C.J. Eyermann, J. Hopkins, H.T. Lee, D. Seyferth, H.P. Withers and W.L. Jolly, Organometallics, 1 (1982) 699.
30 Efforst to obtain crystals of this molecule suitable for X-ray analysis are continuing in these laboratories.
31 S.B. Colbran, B.H. Robinson and J. Simpson, Acta Crystallogr., C42 (1986) 972.