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Contribution from the Institut Le Bel, Université Louis Pasteur, 67070 Strasbourg, France,
the Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR,
43100 Parma, Italy, and the Istituto di Chimica Generale ed Inorganica, Università di Torino, 10125 Torino, Italy

Synthesis and Structural Characterization of a New Chromium–Iron–Sulfur Cluster, $(\eta^5\text{-}C_5H_5)_2Cr_2Fe_2(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2(CO)_6$

PIERRE BRAUNSTEIN,*[1a] ANTONIO TIRIPICCHIO, MARISA TIRIPICCHIO CAMELLINI,[1b]
and ENRICO SAPPA[1c]

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The reaction of $Fe_2(CO)_6S_2$ with $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ affords the new heterotetrametallic cluster $(\eta^5\text{-}C_5H_5)_2Cr_2Fe_2(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2(CO)_6$ (complex IV). Its X-ray analysis shows a butterfly arrangement for the Cr_2Fe_2 core; the two chromium atoms occupy the hinge, with a Cr–Cr bond distance of 2.775 (4) Å, and the two iron atoms are on the tops of the wings, with average Cr–Fe bond distances of 2.762 (3) Å. One Cp ring is η^5 bonded to each chromium atom, and three CO ligands are terminally bonded to each iron atom. Two carbonyls triply bridge very asymmetrically one Cr and two Fe atoms (IR: ν(CO) 1765 cm^{-1}) (Cr–C = 1.87 (1) Å and Fe–C = 2.53 (1) Å) which is unusual for an open trimetallic ensemble. Two S atoms triply bridge the two triangular $FeCr_2$ faces with Cr–S and Fe–S average distances of 2.230 (4) and 2.160 (5) Å, respectively. Crystallographic details for complex IV are as follows: space group *Pmmn* (orthorhombic), $a = 15.59$ (2) Å, $b = 15.59$ (2) Å, $c = 8.65$ (1) Å, $V = 2102$ (4) $Å^3$, $Z = 4$, ρ(calcd) = 2.003 g cm^{-3}, and μ(Mo Kα) = 25.72 cm^{-1}. The final *R* factor was 4.1% anisotropic for 1184 observed reflections ($I > 2\sigma(I)$).

Heterometallic derivatives are now a quite common item in the metal–carbonyl cluster chemistry.[2a] However, the mechanisms leading to these derivatives are still unclear, and much work is needed in order to rationalize synthetic methods.

We obtained several new mixed iron–nickel complexes by reacting nickelocene or binuclear nickel cyclopentadienyl derivatives with mono- and trinuclear iron derivatives;[2b–d] these reactions showed low selectivity, and a better explanation for the observed results was "metal fragment condensation" favored by the presence of alkyne ligands.

In order to gain a deeper insight into the ligand-assisted formation of some heterometallic clusters, we undertook a study of the reactivity of structurally different bimetallic iron derivatives, e.g., $Fe_2(CO)_9$, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, $Fe_2(CO)_6S_2$, and $Fe_2(CO)_6(SR)_2$, toward organometallic complexes potentially capable of condensing with the diiron units.

We already reported the reaction of $Fe_2(CO)_6S_2$ (complex I) with $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$, yielding $(\eta^5\text{-}C_5H_5)_2Ni_2Fe(\mu_3\text{-}S)(CO)_3$ (complex II).[3] Complex I undergoes Fe–Fe and S–S bond breaking also in the presence of $Co_2(CO)_8$, forming $Co_2Fe(\mu_3\text{-}S)(CO)_9$;[4] recently Seyferth and co-workers[5,6] inserted several monometallic derivatives of Ni, Pd, Pt, and Co into the S–S bond of complex I under mild conditions, without Fe–Fe bond cleavage.

We now report the reaction of complex I with $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ (complex III). On the basis of the above evidence, one could expect both Fe–Fe and S–S bond cleavage and formation of trinuclear mixed derivatives. Instead, this reaction leads to the tetrametallic cluster $(\eta^5\text{-}C_5H_5)_2Cr_2Fe_2(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2(CO)_6$ (complex IV). To our knowledge, complex IV is the first tetranuclear chromium–iron cluster, the trimetallic $(CO)_5CrFe_2(CO)_6(\mu_3\text{-}PPh)$[7] being probably the only other reported iron–chromium cluster.

Experimental Section

Materials. Bis(tricarbonyliron sulfide)[8] and bis(cyclopentadienyltricarbonylchromium)[9] were prepared according to literature methods. All operations were carried out in Schlenk flasks under a nitrogen atmosphere. Solvents were distilled under nitrogen, over sodium wire, before use.

Synthesis and analysis of Complex IV. A mixture of $Fe_2(CO)_6S_2$ (0.350 g, 1.02 mmol) and $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ (0.500 g, 1.03 mmol) was stirred in a mixture of hexane–toluene (50 mL:25 mL). After 30 min of refluxing, the black solution was evaporated to dryness and the residual chromatographed on silicagel column.

Elution with toluene–pentane (10:100 v/v) afforded a red-violet band, which was collected. Mass spectral (chemical ionization), infrared, and microanalytical results showed that this product is $Fe_3(CO)_9S_2$; the formulation $Fe_3(CO)_{10}S$ is excluded because of the lack of bridging carbonyl absorptions in the IR spectra.

Further elution with toluene–pentane (50:50 v/v) afforded a dark brown-green solution which was evaporated under vacuum. The product was recrystallized in toluene–pentane and afforded green-black single crystals of IV which were collected and dried (0.03 g; 5% yield based on Cr). Anal. Calcd for IV: C, 34.10; Cr, 16.40; Fe, 17.61; H, 1.59; O, 20.19; S, 10.11. Found: C, 34.18; Cr, 16.18; Fe, 18.00; H, 1.70; S, 10.40. Complex IV decomposed in the mass spectrometer, and, instead of the expected *m/e* 634 parent ion, mixed-metal ions of lower weight (isotopic pattern Cr_2Fe_2, Cr_2Fe, and $CrFe_2$) were observed, together with loss of CO and sulfur and, probably, of COS groups.

X-ray Data Collection. A green-black crystal of approximate dimensions ca. 0.15 × 0.18 × 0.25 mm was used for the structure determination. It was mounted on a glass fiber on a eucentric head. Preliminary cell dimensions and the possible space groups were determined from oscillation and Weissenberg photographs. The zero-level Weissenberg photograph indicated D_{4h} Laue symmetry, the upper levels D_{2h} Laue symmetry. Systematic absences (*hk*0 reflections with $h + k = 2n + 1$) are compatible with the orthorhombic space groups *Pmmn* and $Pm2_1n$. The crystal was transferred to a Siemens AED single-crystal diffractometer, with the *c* axis along the Φ axis of the diffractometer. Refined cell parameters were obtained by a least-squares treatment of θ values for 14 reflections accurately measured with Mo Kα radiation. The crystal data are as follows from systematic absences and structure determination: $C_{18}H_{10}Cr_2Fe_2O_8S_2$, mol wt = 634.08, orthorhombic, $a = 15.59$ (2) Å, $b = 15.59$ (2) Å, $c = 8.65$ (1) Å, $V = 2102$ (4) $Å^3$, $Z = 4$, ρ(calcd) = 2.003 g cm^{-3}, μ(Mo Kα) = 25.72 cm^{-1}, space group: *Pmmn* (origin at *mmn*).

A complete set of intensity data was collected, at room temperature, with θ in the range $3 < \theta < 24°$ on the same diffractometer using

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Table I

Fractional Atomic Coordinates ($\times 10^4$) of the Nonhydrogen Atoms[a]

	x/*a*	*y*/*b*	*z*/*c*
Fe1	1184 (1)	0	1701 (2)
Fe2	5000	1187 (1)	4904 (2)
Cr1	0	890 (1)	−51 (2)
Cr2	4110 (1)	0	6649 (3)
S1	1044 (2)	0	−790 (4)
S2	5000 (1)	1042 (2)	7380 (4)
O1	950 (7)	0	5063 (11)
O2	2381 (5)	1435 (5)	1710 (11)
O3	0	1503 (7)	3211 (12)
O4	5000	948 (7)	1565 (15)
O5	3589 (5)	2425 (5)	4926 (11)
O6	3523 (6)	0	3367 (11)
C1	1004 (8)	0	3757 (19)
C2	1921 (6)	863 (7)	1746 (12)
C3	0	1088 (9)	2067 (17)
C4	5000	1022 (8)	2836 (14)
C5	4135 (6)	1947 (6)	4890 (12)
C6	3922 (8)	0	4485 (17)
C7	0	1595 (9)	−2245 (21)
C8	730 (7)	1842 (6)	−1418 (14)
C9	448 (7)	2241 (5)	−50 (15)
C10	3399 (8)	0	8870 (18)
C11	3146 (6)	731 (8)	7997 (15)
C12	2759 (6)	452 (7)	6606 (14)

Calculated Fractional Atomic Coordinates for the Hydrogen Atoms ($\times 10^4$)

	x/*a*	*y*/*b*	*z*/*c*
H(7)	0	1266	−3345
H(8)	1387	1744	−1765
H(9)	853	2502	846
H(10)	3720	0	9976
H(11)	3235	1394	8340
H(12)	2508	862	5704

[a] Estimated standard deviations in parentheses.

niobium-filtered Mo Kα radiation ($\lambda = 0.710\,69$ Å) at a takeoff angle of 4°. The pulse height discriminator was set to accept 90% of the Mo Kα peak radiation. The $\theta/2\theta$ scan technique was used with a variable-scan rate ranging from 2.5 to 10°/min. Scan range was ±0.5 from peak center. A standard reflection measured after every 20 reflections as a check on crystal and instrument stability showed no significant change in the measured intensities during data collection. For the determination of intensities and background, the five-point technique[10] was used. A total of 1782 independent reflections were measured of which 1184 having $I > 2\sigma(I)$ [$\sigma^2(I)$ = total counts + $(0.01(\text{intensity}))^2$] were used in the analysis. The remaining 598 were considered unobserved. The structure amplitudes were obtained after the usual Lorentz and polarization corrections, and the absolute scale was established by Wilson's method, which also yielded the overall temperature factor. No absorption corrections were applied, in view of the small size of the crystal and of the low linear absorption coefficient.

Solution and Refinement of the Structure. Initial positional parameters of the heavy atoms were determined from a Patterson map. A Fourier map calculated with phases of these atoms revealed the positions of all other nonhydrogen atoms. Refinement was carried out by full-matrix least squares[11] isotropically to $R = 8.1\%$ and anisotropically to $R = 4.3\%$. The hydrogen atoms could not be precisely located in a difference Fourier and were placed in their geometrically calculated positions with uniform isotropic thermal parameters ($U = 0.07$ Å^2) in the final structure factor calculation ($R = 4.1\%$; observed reflections only). The function minimized during the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$; unit weights were chosen at each stage of the refinement after analyzing the variation of ΔF with respect to $|F_o|$. The analytical scattering factors for neutral chromium, iron, sulfur, oxygen, carbon, and hydrogen were used throughout the analysis; both the real and imaginary components of anomalous dispersion were included for chromium, iron, and sulfur atoms.[12] The final positional parameters for the nonhydrogen atoms and for the hydrogen atoms are given in Table I. Atomic thermal parameters for the nonhydrogen atoms are reported in Table II.

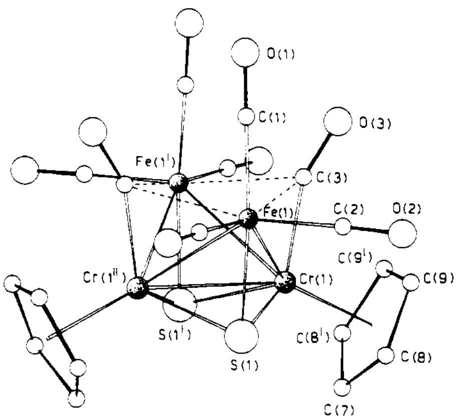

Figure 1. View of the molecular shape of an independent complex with the atomic numbering scheme.

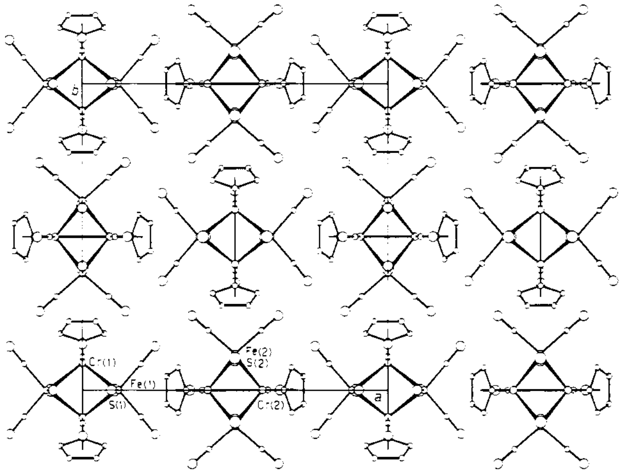

Figure 2. Projection of the crystal structure along the *c* axis.

All calculations were performed on the Cyber 7600 computer of the centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

Discussion

The crystal structure of the title compound consists of two essentially identical independent complexes of $(\eta^5\text{-}C_5H_5)_2Cr_2Fe_2(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2(CO)_6$ linked to each other by normal van der Waals contacts. Each complex is characterized by a butterfly arrangement of two chromium and two iron atoms, in which the former occupy the "hinge" side and the other are on the tops of the "wings"; two sulfur atoms triply bridge the triangular wings (the mean value of the dihedral angle between the wings in the two complexes is 101.3°). The two cyclopentadienyl groups are η^5-bonded to the chromium atoms (the mean distance of the metal atom from the barycentre of the ring is 1.87 (1) Å); three terminal carbonyls are attached to each iron atom, and two carbonyls are asymmetrically triply bridging one chromium and two iron atoms. A view of one of the two independent complexes, with the atomic numbering system, is shown in Figure 1. The Figure 2 represents a projection of the structure along the *c* axis showing a bidimensional square symmetry in agreement with the D_{4h} Laue symmetry of the zero-level photograph.

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Table II. Anisotropic Thermal Parameters for the Nonhydrogen Atoms[a, b]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	2.44 (8)	3.93 (9)	2.69 (9)	0	−0.32 (8)	0
Fe(2)	3.13 (8)	2.52 (8)	2.36 (8)	0	0	−0.13 (7)
Cr(1)	2.58 (8)	1.98 (8)	2.34 (9)	0	0	−0.02 (8)
Cr(2)	1.96 (8)	3.61 (9)	2.59 (9)	0	0.10 (8)	0
S(1)	2.61 (13)	2.77 (13)	2.45 (14)	0	0.35 (12)	0
S(2)	2.73 (13)	3.72 (16)	2.34 (15)	0	0	−0.61 (13)
O(1)	5.14 (61)	12.32 (88)	1.67 (38)	0	−0.71 (43)	0
O(2)	5.35 (41)	6.00 (46)	8.41 (55)	−1.74 (40)	−0.62 (43)	−1.26 (44)
O(3)	5.74 (55)	5.06 (56)	4.48 (53)	0	0	−1.87 (51)
O(4)	12.59 (88)	3.84 (58)	4.30 (65)	0	0	1.15 (53)
O(5)	4.59 (36)	5.12 (37)	7.15 (45)	2.00 (34)	−0.03 (36)	0.22 (37)
O(6)	5.64 (50)	4.62 (49)	3.40 (44)	0	−2.97 (44)	0
C(1)	2.06 (50)	8.03 (99)	4.79 (92)	0	−1.43 (51)	0
C(2)	3.43 (44)	4.57 (51)	3.92 (49)	−0.09 (43)	0.13 (40)	0.03 (46)
C(3)	4.43 (76)	3.19 (61)	3.85 (73)	0	0	−1.00 (55)
C(4)	4.74 (74)	2.27 (55)	1.51 (54)	0	0	0.15 (40)
C(5)	4.02 (46)	3.79 (45)	3.28 (45)	0.02 (43)	−0.41 (39)	0.39 (41)
C(6)	2.75 (50)	3.14 (61)	4.17 (76)	0	−0.17 (50)	0
C(7)	9.22 (1.22)	2.51 (66)	4.97 (97)	0	0	1.82 (64)
C(8)	5.60 (57)	2.94 (42)	6.12 (66)	−1.02 (43)	0.58 (52)	2.04 (45)
C(9)	5.60 (52)	2.19 (37)	6.50 (61)	−0.04 (39)	0.19 (54)	0.45 (47)
C(10)	2.07 (54)	13.95 (1.59)	4.33 (81)	0	2.41 (54)	0
C(11)	2.22 (41)	7.33 (65)	7.71 (78)	0.24 (43)	2.44 (47)	−2.87 (58)
C(12)	1.62 (37)	5.64 (54)	6.37 (62)	0.64 (39)	0.92 (43)	−0.38 (51)

[a] Estimated standard deviations in parentheses. [b] The parameters are in the form $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + \ldots + 2klb^*c^*B_{23})]$.

Each complex possesses a crystallographic imposed C_{2v}—2*mm* symmetry. One mirror plane is determined by the hinge side and the midpoint between the two iron atoms, and the other mirror plane passes through the two iron atoms and the midpoint of the hinge side. Bond distances and angles are given in Table III. The mean value of the Cr–Cr distances, 2.775 (4) Å, is much shorter than in the parent complex III where for the rather long Cr–Cr distance, 3.281 Å, a weak metal-metal bond was postulated.[9]

Very different values for the Cr–Cr distance have been found in dinuclear complexes: in $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_4[P(OMe)_3]_2$[13] and in the arsenido-bridged complex $(\eta^5\text{-}C_5H_5)Cr_2(\mu_2\text{-}AsR_2)(CO)_7$,[14] values of 3.343 and 3.192 Å have been reported, respectively; in the alkyne-bridged complex $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)(Ph_4C_4)$[15,16] and in the nonbridged dimer $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_4$,[17] very short distances have been found, 2.337 Å in the former, and 2.200 and 2.230 Å (for two independent molecules) in the latter, indicating triple metal–metal bonding. The mean value of the Cr–Fe bonds, 2.762 (3) Å, is very close to those found for the Cr–Cr bonds and is shorter than those reported for $(CO)_5CrFe_2(\mu_3\text{-}PPh)(CO)_6$,[7] 2.814 and 2.815 Å, the only other known Cr–Fe mixed cluster. The very long mean value of the Fe–Fe distances, 3.696 (3) Å, agrees with nonbonding interaction between the iron atoms. One cyclopentadienyl ligand is η^5-bonded to each chromium atom, thus there is no cyclopentadienyl exchange during the formation of IV, whereas this sometimes occurs in reactions leading to ruthenium–nickel derivatives.[18] As expected, the C_5H_5 ligands are equivalent and appear as a singlet in the ^{1}H NMR at δ 4.99 (CD_2Cl_2).

Three CO ligands are bound terminally to each iron atom as shown by the Fe–C–O angles ranging from 175 to 178°; the remaining two carbonyls triply bridge very asymmetrically one Cr and two Fe atoms; the presence of the triply bridging CO's could be expected, as the IR spectrum of IV in KBr shows the following bands: 2050 s, 2020 vs, 1989 s, 1980 m, 1971 sh, 1964 s, 1956 sh, and 1765 vs cm^{-1}, the latter being in the expected range for triply bridging CO's (see Table IVA). The bridging carbonyls are mainly associated with the chromium atoms, as shown by the Cr–C mean distance, 1.87 (1) Å, and by the Fe–C mean distance, 2.53 (1) Å.

Table III. Selected Bond Distances (Å) and Angles (Deg) in the Two Independent Molecules[a]

molecule A		molecule B	
Fe(1)–Cr(1)	2.762 (3)	Fe(2)–Cr(2)	2.762 (3)
Fe(1)–S(1)	2.166 (5)	Fe(2)–S(2)	2.154 (5)
Cr(1)–Cr(1)^{II}	2.775 (4)	Cr(2)–Cr(2)^{III}	2.775 (4)
Cr(1)–S(1)	2.232 (4)	Cr(2)–S(2)	2.228 (4)
Cr(1)–C(3)	1.86 (1)	Cr(2)–C(6)	1.89 (1)
Fe(1)–C(1)	1.80 (1)	Fe(2)–C(4)	1.81 (1)
Fe(1)–C(2)	1.77 (1)	Fe(2)–C(5)	1.80 (1)
Fe(1)–C(3)	2.53 (1)	Fe(2)–C(6)	2.53 (1)
Cr(1)–E	1.86 (1)	Cr(2)–F	1.87 (1)
C(1)–O(1)	1.13 (2)	C(4)–O(4)	1.11 (2)
C(2)–O(2)	1.14 (1)	C(5)–O(5)	1.13 (1)
C(3)–O(3)	1.18 (2)	C(6)–O(6)	1.15 (2)
C(7)–C(8)	1.40 (1)	C(10)–C(11)	1.42 (1)
C(8)–C(9)	1.41 (1)	C(11)–C(12)	1.42 (1)
C(9)–C(9)^{I}	1.40 (1)	C(12)–C(12)^{II}	1.41 (1)
Cr(1)–Fe(1)–Cr(1)^{II}	60.3 (1)	Cr(2)–Fe(2)–Cr(2)^{III}	60.3 (1)
Cr(1)–Fe(1)–S(1)	52.2 (1)	Cr(2)–Fe(2)–S(2)	52.1 (1)
Fe(1)–Cr(1)–Fe(1)^{I}	83.9 (1)	Fe(2)–Cr(2)–Fe(2)^{II}	84.1 (1)
Fe(1)–Cr(1)–Cr(1)^{II}	59.8 (1)	Fe(2)–Cr(2)–Cr(2)^{III}	59.8 (1)
Fe(1)–Cr(1)–S(1)^{I}	109.4 (1)	Fe(2)–Cr(2)–S(2)^{II}	109.3 (1)
S(1)–Cr(1)–S(1)^{I}	93.6 (1)	S(2)–Cr(2)–S(2)^{II}	93.6 (1)
Cr(1)–S(1)–Cr(1)^{II}	76.9 (1)	Cr(2)–S(2)–Cr(2)^{III}	77.0 (1)
Fe(1)–S(1)–Cr(1)	77.8 (1)	Fe(2)–S(2)–Cr(2)	78.1 (1)
Fe(1)–C(1)–O(1)	175 (1)	Fe(2)–C(4)–O(4)	178 (1)
Fe(1)–C(2)–O(2)	177 (1)	Fe(2)–C(5)–O(5)	178 (1)
Cr(1)–C(3)–O(3)	156 (1)	Cr(2)–C(6)–O(6)	156 (1)
Fe(1)–C(3)–O(3)	118 (1)	Fe(2)–C(6)–O(6)	119 (1)
Fe(1)–C(3)–Cr(1)	76.4 (4)	Fe(2)–C(6)–Cr(2)	75.8 (4)
Fe(1)–C(3)–Fe(1)^{I}	93.9 (5)	Fe(2)–C(6)–Fe(2)^{II}	94.2 (4)
C(8)^{I}–C(7)–C(8)	109 (1)	C(11)^{II}–C(10)–C(11)	106 (1)
C(7)–C(8)–C(9)	107 (1)	C(10)–C(11)–C(12)	109 (1)
C(8)–C(9)–C(9)^{I}	108 (1)	C(11)–C(12)–C(12)^{I}	108 (1)

[a] E and F are the barycenters of the two cyclopentadienyl rings. Roman superscripts indicate in the following equivalent transformations: (I) $-x, y, z$; (II) $x, -y, z$; (III) $1-x, y, z$.

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Table IV

(A) Some Examples of Asymmetrical Triply Bridging CO's in Mixed-Metal Clusters

complex	M-M and M-M', Å	M-C and M-C', Å[a]	M-C-M and M-C-M', deg[a]	ν_{CO}, cm^{-1}	ref
$Fe_3(\mu_3\text{-}S)(\mu_3\text{-}CO)(CO)_9$	Fe-Fe 2.61 (1)	Fe-C 2.06 (2)		1730[b] (1896.5)[d]	19
$(Cp)_2NiRu_2(\mu_3\text{-}CO)(CO)_3(C_2Ph_2)$	Ru-Ru 2.712 (3)	Ru-C 1.909 (7)	Ru-C-Ru 79.5 (2)	1610,[b] 1640[c]	18
	Ru-Ni 2.550 (3)	2.307 (7)	Ru-C-Ni 75.2 (2)	1780[b,d]	
	2.553 (2)	2.249 (7)	68.1 (2)		
$(Cp)_2Ni_2Fe_2(\mu_3\text{-}CO)(CO)_6$	Fe-Fe 2.530 (2)	Fe-C 1.981 (11)	Fe-C-Fe 79.9 (4)	1722[b]	2
	Ni-Fe 2.408 (2)	1.961 (10)	Fe-C-Ni 72.1 (3)		
	2.411 (2)	Ni-C 2.110 (10)	72.6 (4)		
$(Cp)_2Cr_2Fe_2(\mu_3\text{-}S)_2(CO)_6$	Fe-Fe 3.696 (3)[f]	Fe-C 2.53 (1)[f]	Fe-C-Fe 94.0 (4)[f]	1765[c]	this work
	Fe-Cr 2.762 (3)	Cr-C 1.87 (1)	Cr-C-Fe 76.1 (4)		
	Cr-Cr 2.775 (4)				
$(Cp)_2Cr_2Pd_2(\mu_3\text{-}CO)_2(CO)_4(PEt_3)_2$	Pd-Pd 2.578 (1)	Cr-C 1.925 (8)	Pd-C-Pd 68.0 (2)	1773[c]	
	Pd-Cr 2.741 (1)	Pd-C 2.344 (8)	Pd-C-Cr 81.3 (3)		23
	2.777 (1)	2.264 (7)	80.5 (3)		
$(Cp)_2Mo_2Pd_2(\mu_3\text{-}CO)_2(CO)_4(PEt_3)_2$	Pd-Pd 2.582 (1)	Mo-C 2.038 (6)	Pd-C-Pd 66.7 (1)	1768[c]	
	Pd-Mo 2.827 (1)	Pd-C 2.385 (6)	Pd-C-Mo 80.3 (2)		24
	2.864 (1)	2.307 (5)	80.9 (2)		

(B) Selected Structural Parameters for Some Sulfur Cluster Derivatives Relevant to the Discussion

complex	M-M and M-M', Å	M-S and M'-S, Å	M-S-M and M-S-M', deg	ref
$Fe_2(CO)_6S_2$	Fe-Fe 2.552 (2)	Fe-S 2.228 (2)[g]	Fe-S-Fe 69.9 (1)[g]	8
$Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}CO)$	Fe-Fe 2.61 (1)[g]	Fe-S 2.21 (1)[g]		19
$HFe_3(CO)_9(\mu_3\text{-}S\text{-}i\text{-}C_3H_7)$	Fe-Fe 2.653 (2)	Fe-S 2.136 (2)	Fe-S-Fe 76.39 (9)	20
	2.640 (2)[h]	2.139 (3)	77.18 (9)	
	2.678 (2)[h]	2.154 (2)	76.26 (9)	
$FeCo_2(\mu_3\text{-}S)(CO)_9$	M-M[i] 2.254 (3)[f]	M-S 2.158 (4)[f]	M-S-M 72.5 (2)[f]	4
$(Cp)_2Ni_2Fe(\mu_3\text{-}S)(CO)_3$	Ni-Ni 2.404 (9)	Ni-S 2.109 (5)	Ni-S-Ni 69.4 (1)	3
	Ni-Fe 2.427 (4)	2.114 (5)	Ni-S-Fe 69.0 (2)	
	2.419 (4)	Fe-S 2.158 (6)	69.3 (2)	
$(CO)_5CrFe_2(\mu_3\text{-}PPh)(CO)_6$	Fe-Fe 2.664 (3)			
	Fe-Cr 2.815 (3)			
	2.814 (3)			
$(Cp)_2Cr_2Fe_2(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2(CO)_6$	Fe-Fe 3.696 (3)[f]	Fe-S 2.160 (5)[f]	Cr-S-Cr 77.0 (1)[f]	this work
	Fe-Cr 2.762 (3)	Cr-S 2.230 (4)	Cr-S-Fe 78.0 (1)	
	Cr-Cr 2.775 (4)			
$(CO)_5CrSFeCo_2(CO)_9$	M-M[i] 2.557 (3)	M-S 2.145 (5)		21
		Cr-S 2.351 (5)		

[a] Only the ones interested in the (μ_3-CO). [b] Heptane or hexane solution. [c] KBr. [d] Solution form with (μ_2-CO). [e] Symmetrical bridge. [f] Average values in two independent molecules. [g] Average values. [h] Distance with (μ-H). [i] Average data because of disorder.

Relevant structural features are reported and compared in Table IVA. It is noteworthy that in the present complex the triply bridging CO's are not associated to a closed triangular metal–metal ensemble, as the two CO's bridge one metal in the hinge and the two nonbonded Fe atoms on the wings of the butterfly metal arrangement.

Two sulfur atoms triply bridge the two triangular Cr–Cr–Fe faces: the mean values of the Cr–S and Fe–S distances are 2.230 (4) and 2.160 (5) Å, respectively, the mean nonbonding S–S distance being 3.253 (5) Å. Complexes with triply bridging sulfur atoms are known: the recently reported $Fe_3(CO)_{10}S$,[19] the heterometallic complexes II,[3] and $FeCo_2(CO)_9S$[4] are all characterized by a formally four-electron donor, triply bridging sulfur atom, whereas in $HFe_3(CO)_9(SR)$ (R = $i\text{-}C_3H_7$, $t\text{-}C_4H_9$) the triply bridging SR unit is a formal five-electron donor.[20] The metal–sulfur bonding parameters for IV and other complexes are compared in Table IVB. No other value seems to have been reported for a Cr–S distance in a cluster,[1] in $(CO)_5CrSFeCo_2(CO)_9$, the sulfur atom is bound both to iron and chromium atoms, but this latter is not part of the cluster.[21] Noteworthy in the present complex is the presence both of the triply bridging CO's and of the triply bridging sulfur atoms, as already found in $Fe_3(CO)_{10}S$.[19] When the sulfur atom is considered as a formal four-electron donor, the complex IV shows the butterfly structure expected for a 62-electron cluster.[22] Although some electron delocalization might occur in this cluster, the asymmetry in the μ_3-CO bonding seems mainly related to the mixed nature of the cluster. This emphasizes the interest for the knowledge of the structure of mixed-metal clusters as indicators of the preferential bonding of ligands to competing metal centers.

Finally, in IV there are no Fe–Fe and S–S interactions, thus it can be considered formed by "condensation" of $Fe(CO)_3S$ fragments, obtained by the splitting of I, on the chromium complex III. However, this process would require the cleavage of several S–S, Fe–Fe, and Fe–S bonds in a nonconcerted pathway. More tempting is the hypothesis of the insertion of III or better of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2$, which may be thermally generated in situ from III, in the S–S or Fe–Fe bond of I, followed by rearrangement. This point is presently under investigation in our laboratories.

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Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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