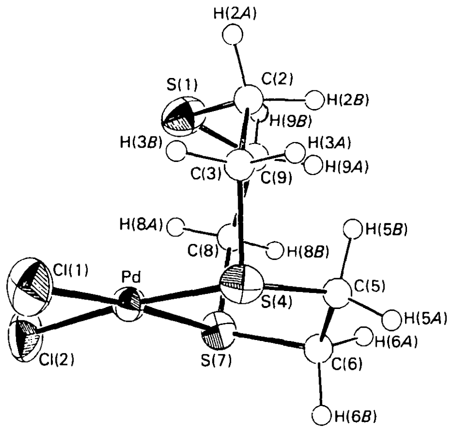


Fig. 1. *ORTEP* plot of the molecule showing atom-labelling scheme. Thermal ellipsoids are shown at the 30% probability level excepting those for C and H, which have artificial radii of 0·15 and 0·10 Å respectively, for clarity.

$S = 1{\cdot}020$ for 109 parameters, $(\Delta/\sigma)_{max} = 0{\cdot}004$, max. $\Delta\rho = +0{\cdot}34$, min. $= -0{\cdot}36$ e Å$^{-3}$. No secondary-extinction parameter. Scattering factors inlaid (Sheldrick, 1976) except for Pd (Cromer & Mann, 1968). Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1 while selected molecular parameters appear in Table 2.* The atom-numbering scheme for the structure is shown in Fig. 1, which was generated using *ORTEP* (Mallinson & Muir, 1985). Molecular-geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

* Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44451 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Related literature.** The corresponding *cis*-[$PdBr_2L$] complex is isostructural (Wieghardt, Küppers, Raabe & Krüger, 1986) with $Pd-S_{eq} = 2{\cdot}275$ (2), 2·257 (2) and $Pd-S_{ax} = 3{\cdot}125$ (1) Å, $\langle S_{eq}PdS_{ax}\rangle = 78{\cdot}7$ (1), 81·7 (1)°. The homoleptic [$PdL_2$]$^{2+}$ cation shows a closer axial interaction [Pd···S = 2·952 (4) Å] and a significantly different ligand conformation (Blake, Holder, Hyde, Roberts, Lavery & Schröder, 1987; Wieghardt *et al.*, 1986).

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# The Structure of Pentacarbonyl-$\mu$-[$\sigma$:$\eta^4$-(1-carbonyl-2-phenyl-2-butenyl)]-($\eta^5$-cyclopentadienyl)diiron(I), [$(CO)_3Fe\{CH_3CHC(C_6H_5)CCO\}Fe(CO)_2Cp$]

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**Abstract.** [$Fe_2(C_5H_5)(C_{11}H_9O)(CO)_5$], $M_r = 474{\cdot}036$, $P2_1/n$, $a = 9{\cdot}254$ (3), $b = 17{\cdot}367$ (3), $c = 12{\cdot}601$ (3) Å, $\beta = 95{\cdot}58$ (2)°, $V = 2015{\cdot}6$ (9) Å$^3$, $Z = 4$, $D_x = 1{\cdot}562$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) $= 0{\cdot}71073$ Å, $\mu = 14{\cdot}71$ cm$^{-1}$, $F(000) = 960$, $T = 298$ (2) K, $R = 0{\cdot}041$ for 2746 unique observed reflections. The most striking feature of this structure is the clear example of a C atom of the vinylketene participating in simultaneous $\sigma$ and $\pi$ bonding to two otherwise unrelated Fe centers. The Fe···Fe interatomic distance of 3·845 (1) Å precludes any metal–metal bonding. There is an apparent lengthening of the Fe—CO bond *trans* to the α-C of the dienone, indicating that the carbonyl end of the dienone is effectively competing as a back acceptor of electron density from the Fe atom. The four allylic C atoms are coplanar with a maximum deviation from the mean plane of 0·05 Å. The vinylketene O atom is 0·52 Å above this mean plane.

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

| | $x$ | $y$ | $z$ | $U_{eq}$*(Å²) |
|---|---|---|---|---|
| Fe1 | 0·64053 (5) | 0·22500 (3) | 0·13722 (4) | 0·0477 (2) |
| Fe2 | 0·27208 (5) | 0·12165 (3) | 0·12845 (4) | 0·0490 (2) |
| C1 | 0·3318 (5) | −0·0556 (3) | 0·1768 (5) | 0·067 (2) |
| C2 | 0·3762 (4) | 0·0136 (2) | 0·1172 (3) | 0·051 (1) |
| C3 | 0·4774 (4) | 0·0694 (2) | 0·1667 (3) | 0·044 (1) |
| C4 | 0·5000 (3) | 0·1380 (2) | 0·1087 (3) | 0·044 (1) |
| C5 | 0·3960 (4) | 0·1432 (2) | 0·0163 (3) | 0·050 (1) |
| O5 | 0·3923 (3) | 0·1585 (2) | −0·0763 (2) | 0·072 (1) |
| C6 | 0·1950 (5) | 0·0957 (3) | 0·2503 (4) | 0·077 (2) |
| O6 | 0·1399 (4) | 0·0799 (3) | 0·3236 (3) | 0·137 (2) |
| C7 | 0·1333 (4) | 0·0925 (2) | 0·0296 (4) | 0·062 (2) |
| O7 | 0·0551 (3) | 0·0734 (2) | −0·0418 (3) | 0·088 (1) |
| C8 | 0·2260 (4) | 0·2203 (3) | 0·1419 (4) | 0·075 (2) |
| O8 | 0·1980 (4) | 0·2840 (2) | 0·1510 (4) | 0·115 (2) |
| C9 | 0·5638 (5) | 0·2545 (3) | 0·2520 (4) | 0·078 (2) |
| O9 | 0·5158 (5) | 0·2756 (2) | 0·3265 (3) | 0·127 (2) |
| C10 | 0·5346 (5) | 0·2891 (3) | 0·0540 (4) | 0·079 (2) |
| O10 | 0·4733 (4) | 0·3333 (2) | −0·0001 (4) | 0·127 (2) |
| C11 | 0·7986 (4) | 0·2052 (3) | 0·0327 (4) | 0·069 (2) |
| C12 | 0·8012 (4) | 0·1452 (3) | 0·1058 (4) | 0·070 (2) |
| C13 | 0·8304 (4) | 0·1749 (3) | 0·2094 (4) | 0·077 (2) |
| C14 | 0·8494 (4) | 0·2561 (3) | 0·1974 (4) | 0·080 (2) |
| C15 | 0·8294 (4) | 0·2747 (3) | 0·0891 (4) | 0·071 (2) |
| C16 | 0·5623 (4) | 0·0520 (2) | 0·2700 (3) | 0·055 (1) |
| C17 | 0·6709 (5) | −0·0032 (2) | 0·2669 (4) | 0·080 (2) |
| C18 | 0·7619 (7) | −0·0179 (4) | 0·3576 (7) | 0·123 (3) |
| C19 | 0·744 (1) | 0·0182 (6) | 0·4511 (7) | 0·145 (4) |
| C20 | 0·6367 (9) | 0·0698 (5) | 0·4550 (4) | 0·121 (3) |
| C21 | 0·5414 (5) | 0·0875 (3) | 0·3648 (3) | 0·075 (2) |

* $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

**Experimental.** Bright red rectangular parallelepipeds, 0·22 × 0·22 × 0·38 mm; Nonius CAD-4 diffractometer, monochromated Mo $K\alpha$; $\theta/2\theta$ scans; $3 \le 2\theta \le 50°$; lattice parameters from 25 high-angle reflections ($2\theta > 20°$); Gaussian integration absorption corrections applied with transmission coefficients 0·71–0·78; $0 \le h \le 10$, $0 \le k \le 20$, $-14 \le l \le 14$; three standard reflections fluctuated 4%; 3610 total reflections, 3527 unique, 2746 observed with $I_o \ge 2\sigma(I)$. Patterson methods; full-matrix refinement *via* *SHELX*76 (Sheldrick, 1976) on $F$'s minimizing $\sum w(F_o - |F_c|)^2$; all non-H atoms anisotropic; most H atoms were placed invariant in calculated geometries and assigned an isotropic thermal parameter equal to 1·5 that of the adjoining C atom; a few H atoms were placed in observed positions and allowed to refine. For observed reflections $R = 0·041$, $wR = 0·047$, $S = 1·56$, $w = (\sigma_F)^{-2}$. Including weak reflections: $R = 0·062$, $wR = 0·054$. In final cycle: $(\Delta/\sigma)_{max} = 0·03$, $(\Delta\rho)_{max} = 0·5$ e Å$^{-3}$ near Fe1, $(\Delta\rho)_{min} = -0·38$ e Å$^{-3}$. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Table 1* gives the atomic coordinates and Table 2 lists selected interatomic distances and angles. Fig. 1 illustrates the geometry and labeling scheme.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares planes and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44341 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| Fe1–C4 | 2·003 (2) | C1–C2 | 1·496 (6) |
| Fe1–C9 | 1·749 (5) | C2–C3 | 1·447 (5) |
| Fe1–C10 | 1·761 (5) | C3–C4 | 1·424 (5) |
| Fe1–C11 | 2·090 (4) | C3–C16 | 1·484 (5) |
| Fe1–C12 | 2·098 (4) | C4–C5 | 1·439 (5) |
| Fe1–C13 | 2·088 (5) | C5–O5 | 1·194 (4) |
| Fe1–C14 | 2·078 (4) | C6–O6 | 1·132 (6) |
| Fe1–C15 | 2·091 (4) | C7–O7 | 1·147 (5) |
| Fe2–C2 | 2·121 (4) | C8–O8 | 1·145 (6) |
| Fe2–C3 | 2·119 (3) | C9–O9 | 1·137 (6) |
| Fe2–C4 | 2·166 (3) | C10–O10 | 1·141 (7) |
| Fe2–C5 | 1·941 (4) | Fe1···Fe2 | 3·845 (1) |
| Fe2–C6 | 1·811 (5) | Fe1–Cp* | 1·712 (4) |
| Fe2–C7 | 1·774 (4) | Fe2–Allyl† | 1·682 (5) |
| Fe2–C8 | 1·778 (5) | | |

| | | | |
|---|---|---|---|
| C4–Fe1–C9 | 93·5 (2) | Allyl–Fe2–C6 | 121·9 (2) |
| C4–Fe1–C10 | 93·2 (2) | Allyl–Fe2–C7 | 112·5 (2) |
| Cp–Fe1–C9 | 125·7 (2) | Allyl–Fe2–C8 | 123·6 (2) |
| Cp–Fe1–C10 | 122·4 (2) | Fe2–C2–C1 | 121·9 (9) |
| Cp–Fe1–C4 | 120·3 (2) | C1–C2–C3 | 121·3 (4) |
| C2–Fe2–C6 | 93·2 (2) | Fe2–C3–C16 | 132·3 (2) |
| C2–Fe2–C7 | 90·2 (2) | C2–C3–C4 | 117·4 (3) |
| C2–Fe2–C8 | 166·9 (2) | C2–C3–C16 | 120·4 (3) |
| C3–Fe2–C6 | 96·8 (2) | C4–C3–C16 | 122·0 (3) |
| C3–Fe2–C7 | 127·6 (2) | Fe2–C4–Fe1 | 134·5 (2) |
| C3–Fe2–C8 | 127·5 (2) | Fe1–C4–C5 | 118·0 (2) |
| C4–Fe2–C6 | 126·7 (2) | Fe1–C4–C3 | 131·6 (2) |
| C4–Fe2–C7 | 127·1 (2) | C3–C4–C5 | 110·3 (3) |
| C4–Fe2–C8 | 97·5 (2) | Fe2–C5–O5 | 142·3 (3) |
| C5–Fe2–C6 | 166·9 (2) | C4–C5–O5 | 139·3 (3) |
| C5–Fe2–C7 | 89·0 (2) | Fe2–C6–O6 | 176·4 (4) |
| C5–Fe2–C8 | 92·8 (2) | Fe2–C7–O7 | 172·6 (4) |
| C6–Fe2–C7 | 101·9 (2) | Fe2–C8–O8 | 179·2 (3) |
| C6–Fe2–C8 | 92·4 (2) | Fe1–C9–O9 | 178·1 (5) |
| C7–Fe2–C8 | 100·3 (2) | Fe1–C10–O10 | 175·8 (4) |

* Cp indicates the centroid of the cyclopentadienyl ring.
† Allyl indicates the midpoint of the allylic C2, C3, C4, C5 atoms.

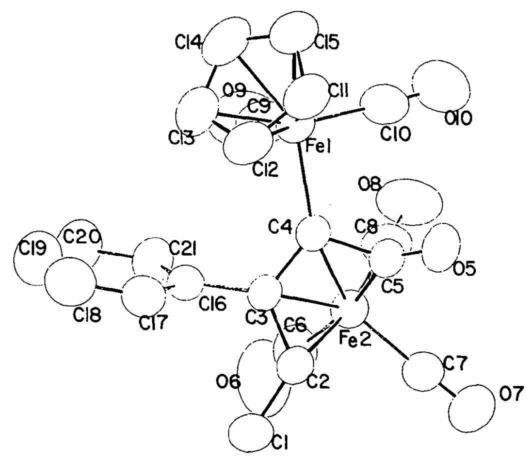


Fig. 1. *ORTEP* (Johnson, 1965) drawing of pentacarbonyl-$\mu$-($\sigma$:$\eta^4$-1-carbonyl-2-phenyl-2-butenyl)-($\eta^5$-cyclopentadienyl)di-iron(I). Ellipsoids are drawn at 50% probability.

**Related literature.** A review of structural patterns in $(CO)_3$Fe(butadiene) complexes has been published (Herbstein & Reisner, 1977). Discussions of the rotational conformations of cyclic (*e.g.* cyclopentadienyl) and acyclic (*e.g.* butadienyl, allylic) $M(CO)_3$ complexes correctly predict the ligand conformations in the title structure (Albright, Hofmann & Hoffmann, 1977; Albright, 1982). Other examples of Fe$(L)_3$-

($\eta^4$-allylcarbonyl) structures, where $L$ = CO or $P(Ph)_3$, are similar to this work and support the assessment of the *trans*-lengthening effect exerted by the α-C atom of the dienone on the Fe—CO lengths (Newton, Pantaleo, King & Chu, 1979; Dettlaf, Behrens & Weiss, 1978; Binger, Cetinkaya & Kruger, 1978; Mitsudo, Sasaki, Watanabe, Takegami, Nishigaki & Nakatsu, 1978; Fischer & Ricard, 1982). A closely related structure contains the ligand $\eta^4$-vinylketenimine (Mitsudo, Watanabe, Komiya, Watanabe, Takaegami, Nakatsu, Kinoshita & Miyagawa, 1980).

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# Structure of ($\eta^5$-Cyclopentadienyl)(dimethyldithiocarbamato)(triphenylphosphine)ruthenium(II)

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**Abstract.** $[Ru(C_3H_6NS_2)(C_5H_5)(C_{18}H_{15}P)]$, $M_r$ = 548·7, triclinic, $P\bar{1}$, $a$ = 10·099 (4), $b$ = 10·373 (3), $c$ = 13·323 (4) Å, α = 98·13 (2), β = 95·91 (3), γ = 115·87 (3)°, $V$ = 1221 (2) Å$^3$, $Z$ = 2, $D_x$ = 1·49 g cm$^{-3}$, λ(Mo $K\alpha$) = 0·71073 Å, μ = 8·7 cm$^{-1}$, $F(000)$ = 560, $T$ = 293 K, $R$ = 0·047 for 1952 unique observed reflections. The dithiocarbamate functions as a bidentate ligand with equal Ru—S distances of 2·395 (3) Å. The two S atoms, the P atom, and the center of the cyclopentadienyl ring approximate a tetrahedral environment for the $Ru^{II}$ ion in contrast to previous Ru-dithiocarbamate structures which have involved six- and seven-coordinate Ru.

**Experimental.** Complex (I) prepared by reaction of $[Ru(HSC_3H_7)(cp)(PPh_3)_2]^+$ with sodium dimethyldithiocarbamate in $CH_2Cl_2$. The thin yellow plate-like crystal used for data collection was obtained by evaporation of a diethyl ether solution. Data crystal 0·02 × 0·28 × 0·44 mm mounted on a glass fiber. Intensities measured with an Enraf–Nonius CAD-4 diffractometer using ω–2θ scans of 4–16° min$^{-1}$ in θ. Unit cell determined from least-squares analysis of angle data for 25 reflections with $17 < 2\theta < 22°$. Analytical absorption correction based on crystal-face measurements varied from 0·79 to 1·00. Data collected to $(\sin\theta)/\lambda$ of 0·55 Å$^{-1}$, $0 < h < 10$, $-10 < k < 10$, $-13 < l < 13$. Three standard reflections (22$\bar{6}$, 41$\bar{4}$, 302) decreased 2·2% over 32·0 h of data collection. 3613 reflections measured, 3384 unique ($R_{int}$ = 0·03), 1432 reflections with $I < 3\sigma(I)$ considered unobserved. Solved by Patterson and Fourier methods. Full-matrix least squares minimized $\sum w(\Delta F)^2$. H atoms constrained to idealized positions with C—H = 0·95 Å and isotropic $B$ value of 1·2 times that of the C atom to which it was bonded. Orientation of the methyl H atoms determined from a difference map. All other atoms refined anisotropically for a total of 280

 