structure determination of $(DMET)_2AuCl_2$ and the variable temperature studies will help to solve the apparent inconsistency.

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References

ALDOSHINA, M. Z., ATOVMYAN, L. O., GOL'DENBERG, L. M., KRASOCHKA, O. N., LYUBOVSKAYA, R. N., LYUBOVSKII, R. B. & KHIDEKEL', M. L. (1986). *Dokl. Akad. Nauk SSSR*, **289**, 1140–1144.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1971). *ORTEP*II. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

KANODA, K., TAKAHASHI, T., KIKUCHI, K., SAITO, K., IKEMOTO, I. & KOBAYASHI, K. (1988). *Synth. Met.* **27**, 385–390.

KIKUCHI, K., HONDA, Y., ISHIKAWA, Y., SAITO, K., IKEMOTO, I., MURATA, K., ANZAI, H., ISHIGURO, T. & KOBAYASHI, K. (1988). *Solid State Commun.* **66**, 405–408.

KIKUCHI, K., IKEMOTO, I. & KOBAYASHI, K. (1987). *Synth. Met.* **19**, 551–554.

KIKUCHI, K., ISHIKAWA, Y., SAITO, K., IKEMOTO, I. & KOBAYASHI, K. (1988*a*). *Acta Cryst.* C**44**, 466–468.

KIKUCHI, K., ISHIKAWA, Y., SAITO, K., IKEMOTO, I. & KOBAYASHI, K. (1988*b*). *Synth. Met.* **27**, 391–396.

KIKUCHI, K., KIKUCHI, M., NAMIKI, T., SAITO, K., IKEMOTO, I., MURATA, K., ISHIGURO, T. & KOBAYASHI, K. (1987). *Chem. Lett.* pp. 551–552.

KIKUCHI, K., MURATA, K., HONDA, Y., NAMIKI, T., SAITO, K., ANZAI, H., KOBAYASHI, K., ISHIGURO, T. & IKEMOTO, I. (1987). *J. Phys. Soc. Jpn*, **56**, 4241–4244.

KIKUCHI, K., MURATA, K., HONDA, Y., NAMIKI, T., SAITO, K., ISHIGURO, T., KOBAYASHI, K. & IKEMOTO, I. (1987). *J. Phys. Soc. Jpn*, **56**, 3436–3439.

KIKUCHI, K., MURATA, K., HONDA, Y., NAMIKI, T., SAITO, K., KOBAYASHI, K., ISHIGURO, T. & IKEMOTO, I. (1987). *J. Phys. Soc. Jpn*, **56**, 2627–2628.

KIKUCHI, K., SAITO, K., IKEMOTO, I., MURATA, K., ISHIGURO, T. & KOBAYASHI, K. (1988). *Synth. Met.* **27**, 269–274.

MURATA, K., KIKUCHI, K., TAKAHASHI, T., KOBAYASHI, K., HONDA, Y., SAITO, K., KANODA, K., TOKIWA, T., ANZAI, H., ISHIGURO, T. & IKEMOTO, I. (1988). *J. Mol. Electron.* **4**, 173–179.

NOGAMI, Y., TANAKA, M., KAGOSHIMA, S., KIKUCHI, K., SAITO, K., IKEMOTO, I. & KOBAYASHI, K. (1987). *J. Phys. Soc. Jpn*, **56**, 3783–3785.

SAKURAI, T. & KOBAYASHI, K. (1979). *Rep. Inst. Phys. Chem. Res.* **55**, 69–77.

Acta Cryst. (1989). C**45**, 575–579

Structures of Two Fe—S Cluster Complexes and Comparisons of Structures of Eight Fe—S Cluster Complexes $(\mu\text{-}R^1S)(\mu\text{-}R^2S)Fe_2(CO)_6$

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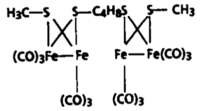
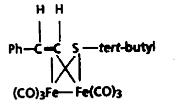
Abstract. (1) μ-1,4-Butanedithio-bis(μ-methylthio-hexacarbonyldiiron), $[(CH_3S)Fe_2(CO)_6S]_2C_4H_8$, $M_r = 773\cdot95$, monoclinic, $P2_1/a$, $a = 7\cdot910\,(1)$, $b = 12\cdot564\,(2)$, $c = 14\cdot644\,(2)$ Å, $\beta = 101\cdot28\,(1)°$, $V = 1427\cdot2$ Å^3, $Z = 2$, $D_x = 1\cdot801$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0\cdot71073$ Å, $\mu = 23\cdot286$ cm^{-1}, $F(000) = 772$, $T = 296$ K, $R = 0\cdot035$ for 890 reflections. (2) μ-Phenylvinyl-μ-*tert*-butylthio-hexacarbonyldiiron, $[(C_4H_9S)Fe_2(C_2H_2C_6H_5)(CO)_6]$, $M_r = 472\cdot08$, monoclinic, $P2_1/n$, $a = 15\cdot145\,(2)$, $b = 9\cdot151\,(1)$, $c = 16\cdot198\,(2)$ Å, $\beta = 113\cdot45\,(1)°$, $V = 2057\cdot8$ Å^3, $Z = 4$, $D_x = 1\cdot52$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0\cdot71073$ Å, $\mu = 15\cdot350$ cm^{-1}, $F(000) = 960$, $T = 296$ K, $R = 0\cdot075$ for 1337 reflections. The influences of the different substituents R^1 and R^2 on the structures of eight Fe—S cluster complexes, $(\mu\text{-}R^1S)(\mu\text{-}R^2S)Fe_2(CO)_6$, were studied. The Fe—Fe distances are almost constant (2·505–2·542 Å). The average Fe—S distances in these complexes are also close to each other (2·250–2·270 Å). Mössbauer spectroscopy of (2) has established that two Fe atoms in this compound have the same coordination environment, so probably one of the Fe atoms is bonded to the π-electrons of the ethylene. In each complex, Fe atoms keep a six-coordinate geometry. The conformations of R^1 and R^2 are (*a*,*e*) type for the majority of these complexes.

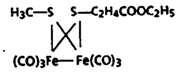
Introduction. Iron–sulfur proteins play an important role in the life sciences, and therefore the investigation of Fe—S cluster complexes is an active field in inorganic and organometallic chemistry. A series of synthesis methods and structures of this kind of complex have been reported (Dahl & Wei, 1963; Wei & Dahl, 1965; Colemon, Wojcicki, Pollick & Dahl, 1967; Seyferth & Womack, 1982; Mak, Book, Chieh, Gallagher, Song & Seyferth, 1983; Song, Hu, Liu, Yang & Wang, 1987). Here, eight structures of Fe—S cluster complexes, $(\mu\text{-}R^1S)(\mu\text{-}R^2S)Fe_2(CO)_6$, are compared and the influences of different substituents R^1 and R^2 on the structures examined. These structures are determined by X-ray diffraction method, in which two structures, (1) and (2), are original and the others have been published or are to be published elsewhere (Wang, Song, Wang & Hu, 1987; Wang, Song, Yao & Hu, 1987; Yao, Song, Wang, Liu, Wang & Wang, 1987; Song, Kadiata, Wang, Wang & Wang, 1988; Song, Wang, Hu & Wang, 1988). Their structural formulas are given below.



(1)



(2)



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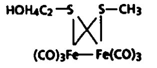
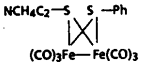


(4)



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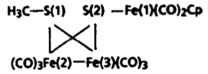
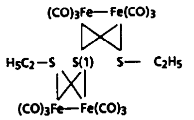
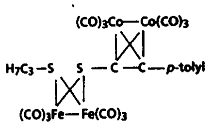


(6)



(7)



(8)

Experimental. The compounds (1) and (2) were prepared as described elsewhere (Song, Kadiata, Hu & Wang, 1988; Song, Liu, Liu, Wang, 1988).

Crystal data (1). Dark red prism, dimensions 0·4 × 0·3 × 0·2 mm, Enraf–Nonius CAD-4 diffractometer, cell constants from 25 reflections with $12 \leq 2\theta \leq 26°$. Data collection using ω–2θ scans, $2 \leq \theta \leq 25°$, $-9 \leq h \leq 9$, $0 \leq k \leq 14$, $0 \leq l \leq 17$. Three standard reflections every 3600 s X-ray exposure time; no decay. Lp correction and empirical absorption correction based on ψ-scans were applied. 890 of the 2631 unique reflections with $F_o^2 \geq 3\sigma(F_o^2)$ used in the refinement. Fe-atom positions found from direct methods (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), other non-hydrogen atoms from successive difference Fourier maps. H atoms included at calculated positions. Final full-matrix least-squares refinement on F (890 reflections, 172 parameters, non-H atoms anisotropic, H atoms isotropic and not refined) resulted in $R = 0{\cdot}035$, $wR = 0{\cdot}043$, $S = 2{\cdot}36$. Unit weights were assigned for each observed reflection. $(\Delta/\sigma)_{\max} = 0{\cdot}15$, $(\Delta\rho)_{\max} = 0{\cdot}46$ e Å^{-3}. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Programs CAD-4 *SDP* (Frenz, 1978) run on a PDP11/44 computer.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses for compounds* (1) *and* (2)

$$B_{eq} = \tfrac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\cos\gamma B(1,2) + ac\cos\beta B(1,3) + bc\cos\alpha B(2,3)].$$

	x	y	z	B_{eq}
Compound (1)				
Fe(1)	0·1665 (2)	0·0758 (1)	0·1778 (1)	3·16 (3)
Fe(2)	0·0552 (2)	−0·0413 (1)	0·2919 (1)	3·42 (3)
S(1)	0·0900 (4)	−0·0966 (2)	0·1497 (2)	3·51 (6)
S(2)	0·3350 (4)	0·0006 (2)	0·3026 (2)	3·37 (6)
C(11)	0·309 (2)	0·096 (1)	0·0949 (8)	4·4 (3)
C(12)	−0·038 (2)	0·1122 (9)	0·1078 (7)	3·7 (3)
C(13)	0·190 (2)	0·204 (1)	0·2289 (8)	4·6 (3)
O(11)	0·395 (1)	0·1041 (9)	0·0425 (6)	7·4 (3)
O(12)	−0·168 (1)	0·1381 (8)	0·0675 (6)	6·5 (3)
O(13)	0·203 (1)	0·2860 (7)	0·2628 (6)	6·5 (3)
C(21)	0·077 (2)	−0·166 (1)	0·3571 (8)	4·7 (3)
C(22)	0·024 (2)	0·050 (1)	0·3801 (8)	4·3 (3)
C(23)	−0·171 (2)	−0·044 (1)	0·2442 (8)	5·0 (3)
O(21)	0·095 (2)	−0·2426 (8)	0·3955 (7)	8·3 (3)
O(22)	0·006 (1)	0·1115 (8)	0·4349 (6)	7·2 (3)
O(23)	−0·316 (1)	−0·0424 (9)	0·2149 (8)	8·1 (3)
C(1)	0·421 (2)	0·095 (1)	0·3960 (8)	5·0 (3)
C(2)	0·546 (2)	0·032 (1)	0·4745 (8)	7·2 (4)
C(3)	0·274 (2)	−0·186 (1)	0·1537 (9)	4·9 (3)
Compound (2)				
Fe(1)	0·2414 (2)	0·2889 (3)	0·9588 (2)	4·14 (6)
Fe(2)	0·4124 (2)	0·2513 (3)	1·0711 (2)	4·38 (6)
S	0·2910 (3)	0·3126 (5)	1·1104 (3)	4·4 (1)
C(1)	0·229 (1)	0·248 (2)	0·856 (1)	5·4 (4)
C(2)	0·284 (1)	0·459 (2)	0·940 (1)	5·3 (5)
C(3)	0·114 (1)	0·319 (2)	0·931 (1)	7·1 (6)
C(4)	0·483 (1)	0·415 (2)	1·109 (1)	6·0 (5)
C(5)	0·474 (1)	0·213 (2)	1·006 (1)	4·6 (5)
C(6)	0·481 (1)	0·140 (3)	1·159 (1)	7·3 (6)
O(1)	0·2211 (9)	0·212 (2)	0·7789 (8)	7·8 (4)
O(2)	0·3097 (9)	0·569 (1)	0·921 (1)	7·3 (4)
O(3)	0·0352 (8)	0·336 (2)	0·913 (1)	9·4 (5)
O(4)	0·5316 (9)	0·514 (1)	1·133 (1)	8·4 (5)
O(5)	0·5132 (9)	0·182 (2)	0·9586 (9)	7·2 (4)
O(6)	0·521 (1)	0·059 (2)	1·216 (1)	10·3 (6)
C(11)	0·320 (1)	0·097 (2)	0·998 (1)	5·8 (5)
C(12)	0·232 (1)	0·057 (2)	1·006 (1)	4·7 (5)
C(13)	0·168 (1)	−0·058 (2)	0·949 (1)	4·1 (4)
C(14)	0·175 (1)	−0·114 (2)	0·873 (1)	5·4 (5)
C(15)	0·112 (1)	−0·228 (2)	0·825 (1)	6·3 (6)
C(16)	0·044 (1)	−0·276 (2)	0·855 (1)	5·8 (5)
C(17)	0·036 (1)	−0·218 (2)	0·928 (1)	6·9 (6)
C(18)	0·097 (1)	−0·108 (2)	0·974 (1)	5·5 (5)
C(21)	0·287 (1)	0·491 (2)	1·165 (1)	5·5 (5)
C(22)	0·304 (1)	0·627 (2)	1·120 (1)	6·4 (6)
C(23)	0·192 (1)	0·493 (2)	1·171 (2)	8·0 (6)
C(24)	0·363 (2)	0·476 (3)	1·260 (1)	7·9 (7)

Crystal data (2). Dark red prism, dimensions 0·3 × 0·3 × 0·2 mm, cell constants from 23 reflections with $12 \leq 2\theta \leq 24°$. Intensity data of the reflections, $-18 \leq h \leq 18$, $0 \leq k \leq 10$, $0 \leq l \leq 19$, were collected. The other conditions were the same as for compound (1). 1337 of the 3855 unique reflections with $F_o^2 \geq 3\sigma(F_o^2)$ used in the refinement. Fe-atom positions

Table 2. *Selected intramolecular distances* (Å)

Compound	Fe—Fe bond	Fe—S bond		S···S distance
(1)	2·511 (2)	Fe(1)–S(1)	2·265 (2)	
		Fe(2)–S(1)	2·262 (2)	
		Fe(1)–S(2)	2·248 (2)	2·926 (4)
		Fe(2)–S(2)	2·251 (2)	
		Ave.	2·256 (1)	
(2)	2·526 (2)	Fe(1)–S	2·270 (3)	S···C11
		Fe(2)–S	2·246 (3)	2·83 (2)
		Ave.	2·258 (2)	
		Fe(1)–C(11)	2·08 (3)	S···C12
		Fe(2)–C(11)	2·010 (9)	2·82 (2)
		Fe(1)–C(12)	2·280 (9)	
(3)	2·518 (3)	Fe(1)–S(1)	2·243 (4)	
		Fe(2)–S(1)	2·247 (3)	
		Fe(1)–S(2)	2·263 (4)	2·916 (4)
		Fe(2)–S(2)	2·248 (3)	
		Ave.	2·250 (2)	
(4)	2·509 (4)	Fe(1)–S(1)	2·256 (6)	
		Fe(2)–S(1)	2·247 (5)	
		Fe(1)–S(2)	2·250 (8)	2·808 (8)
		Fe(2)–S(2)	2·259 (7)	
		Ave.	2·253 (3)	
(5)	2·518 (2)	Fe(1)–S(1)	2·244 (3)	
		Fe(2)–S(1)	2·263 (4)	
		Fe(1)–S(2)	2·262 (3)	2·911 (4)
		Fe(2)–S(2)	2·275 (3)	
		Ave.	2·261 (2)	
(6)	2·505 (3)	Fe(2)–S(1)	2·252 (3)	
		Fe(3)–S(1)	2·257 (4)	
		Fe(2)–S(2)	2·285 (4)	2·881 (4)
		Fe(3)–S(2)	2·285 (4)	
		Ave.	2·270 (2)	
		Fe(1)–S(2)	2·310 (1)	
(7)	Fe(1)–Fe(2)	Fe(1)–S(1)	2·245 (2)	S(1)···S(2)
		Fe(2)–S(1)	2·240 (2)	2·825 (3)
	2·542 (2)	Fe(1)–S(2)	2·275 (2)	S(1)···S(3)
		Fe(2)–S(2)	2·259 (3)	2·812 (3)
	Fe(3)–Fe(4)	Fe(3)–S(1)	2·254 (2)	
		Fe(4)–S(1)	2·244 (2)	
	2·538 (2)	Fe(3)–S(3)	2·270 (2)	
		Fe(4)–S(3)	2·264 (3)	
		Ave.	2·256 (1)	
(8)	2·511 (2)	Fe(1)–S(1)	2·267 (2)	
		Fe(2)–S(1)	2·277 (2)	2·921 (2)
		Fe(1)–S(2)	2·240 (2)	
		Fe(2)–S(2)	2·251 (2)	
		Ave.	2·258 (1)	

found from Patterson map, other non-hydrogen atoms from successive difference Fourier maps. Final full-matrix least-squares refinement on F (1337 reflections, 244 parameters) resulted in $R = 0{\cdot}075$, $wR = 0{\cdot}081$, $S = 4{\cdot}02$, $(\Delta/\sigma)_{\max} = 0{\cdot}08$, $(\Delta\rho)_{\max} = 0{\cdot}65$ e Å^{-3} except for three ghost peaks around the Fe atoms. The comparatively large R factor results from the fact that the prescan speed in collecting the intensity data was too fast (5·49° min^{-1}), so only one third of the unique reflections have significant intensity.

The final atomic coordinates and equivalent isotropic temperature factors for (1) and (2) are listed in Table 1.* Figs. 1 and 2 are perspective views of the two compounds and show the atom-labelling schemes and their conformational features. Selected intramolecular distances of the eight compounds are given in Table 2.

Discussion. As shown in Table 2, the Fe—Fe distances are distributed in a narrow range (2·505–2·518 Å) except for those of (2) and (7). This means that the Fe—Fe bond is not affected by changing the substituents on the S atoms. However, the Fe—Fe bonds are somewhat affected when the composition of the cluster skeleton is different [*e.g.* in compound (2)] or the electron-donating feature of the S atom in the Fe_2S_2 skeleton is different [*e.g.* S(1) in compound (7) donates six electrons to four Fe atoms].

As also shown in Table 2, the average Fe—S distances in these compounds are close to each other (2·250–2·270 Å); it is clear that the Fe—S bonds are also not affected by changing the substituents R^1 and R^2. From the IS values of Mössbauer spectroscopy and the g values of EPR for compound (6), it can be proved

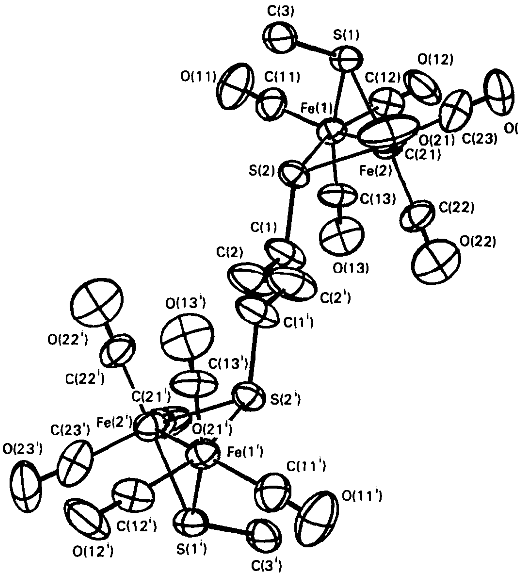


Fig. 1. *ORTEP* (Johnson, 1965) drawing of compound (1). There exists a crystallographic inversion centre at the midpoint of the bond C(2)—C(2').

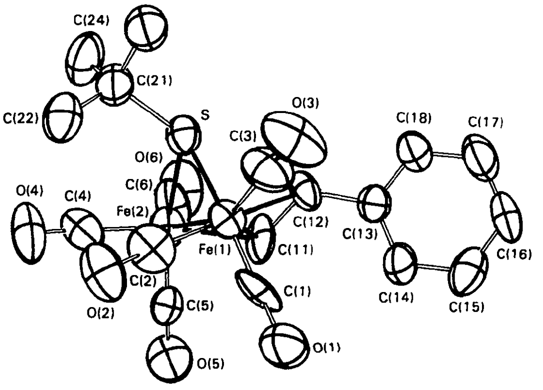


Fig. 2. *ORTEP* (Johnson, 1965) drawing of compound (2).

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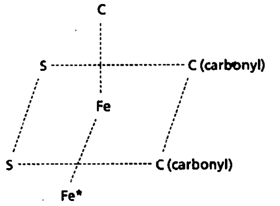
* Lists of structure factors, anisotropic thermal parameters, H-atom positions and interatomic distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51290 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

that Fe(1) is a low-spin iron(III) atom, but Fe(2) and Fe(3) are iron(II) atoms (Zhang, 1987). Although the radius of iron(III) is smaller than that of iron(II), the Fe(1)—S(2) bond length (2·310 Å) is obviously larger than the average bond length (2·250 Å) of the other two Fe—S bonds in (6). It follows therefore that the metal–ring bond formed by Fe(1) and cyclopentadienyl is quite strong, so the Fe(1)—S(2) bond is extended remarkably.

The localized coordination environment about each Fe is a six-coordinate distorted octahedron formed by three carbonyl groups, two S atoms and the other Fe atom. It is sketched below. The Fe atoms are displaced by 0·339–0·410 Å from their respective basal planes in the direction of their apical carbonyl groups. The Fe—C (apical carbonyl) bonds are nearly perpendicular to the basal planes (deviations are only 0·4–4·8°). The departures of Fe—Fe bonds from the normals of their respective basal planes are remarkable, 23·1–27·1°.



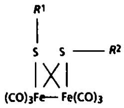
Compound (2) is different in that one of the S atoms in the cluster skeleton is replaced by an ethylene. The Mössbauer spectroscopy of (2) shows one group of double peaks, having IS = 0·262 (2), QS = 0·884 (4), and $\chi = 1 \cdot 901$ (measured by Professor J. K. Zhang, Central Laboratory, Nankai University). This reveals that the two Fe atoms in (2) should have the same coordination environment. According to the result of structure determination, the ethylene formed by C(11) and C(12) takes the position close to Fe(1); it therefore seems that Fe(1) is seven-coordinate and Fe(2) is six-coordinate (see Table 2). However, the fact that the Fe(2) atom lies on the plane through C(11), C(12), C(13), and also that the bond angle Fe(2)—C(11)—C(12) is 125·5°, shows that bond Fe(2)—C(11) is a σ-bond, and the fact that the dihedral angle between the above plane and the plane through Fe(1), C(11), C(12) is relatively large (64·4°) suggest that the Fe(1) atom in compound (2) is probably bonded with the π-electrons of the ethylene formed by C(11) and C(12), so that the Fe(1) and Fe(2) atoms in (2) all still keep a six-coordinate geometry. But the calculation of least-squares planes and dihedral angles for (2) shows that the degree of distortion from a regular octahedron about each of the Fe atoms in (2) differs from those of the other compounds.

The S···S non-bonding distances for the eight complexes vary in the range 2·808–2·926 Å (see Table 2), and it appears that the open angles of the 'butterfly wing' are not determined by the dimensions of the substituents R^1 and R^2 which goes beyond our original understanding of it (Yao, Song, Wang, Liu, Wang & Wang, 1987).

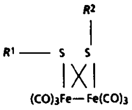
The fact that the Fe—C(carbonyl) distances (1·646–1·827 Å) are obviously shorter than the Fe—C(ethylene) distances (2·009–2·282 Å) in (2) seems to show that there might be electron back-donation in Fe—C(carbonyl) bonds.

The six carbonyls bonded with two Fe atoms always appear in the eclipsed conformation owing to the steric obstruction effect of the S atoms; it has been disturbed partially in (2) because of the substitution of the ethylene for one of the S atoms. The torsion angle of C(3)—Fe(1)—Fe(2)—C(6) in (2) is 55·3°.

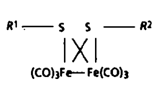
As the substituents R^1 and R^2 are not the same in these complexes, four possible conformers, *ae, ea, ee, aa,* for each complex may exist.



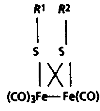
ae



ea



ee



aa

However, except for $(\mu\text{-HS})_2Fe_2(CO)_6$ which can exist as an *aa* conformer (Song, Hu, Liu & Wang, 1985), any complex containing a group larger than hydrogen cannot remain as an *aa* conformer owing to steric hindrance. It has been confirmed by ^{1}H NMR that there are simultaneously three or two types of conformers in solution for this kind of complex (Song, Hu, Liu, Yang & Wang, 1987). The conformation of R^1 and R^2, however, for these complexes in the crystal state is alternatively (*a,e*) or (*e,a*) type; and of the R^1 and R^2 substituents, the larger always takes the conformer with the *a*-type bond except for compounds (1) and (4). Maybe this is favourable for decreasing the exclusion effect between the substituents. In crystals of compound (4), the bond between the ethoxyl and the S atom is an *e*-type bond. The methyl is disordered and occupies two sites: one is *e*-type with a probability of 80% and the other is *a*-type, 20%. The reason that the larger ethoxyl in (4) does not take the *a*-type bond and does take the *e*-type bond is that this conformation is favourable for the formation of an intermolecular hydrogen bond between the hydroxyls (O···O 2·717 Å).

References

COLEMON, J. M., WOJCICKI, A., POLLICK, P. J. & DAHL, L. F. (1967). *Inorg. Chem.* **6**, 1236–1242.

DAHL, L. F. & WEI, C. H. (1963). *Inorg. Chem.* **2**, 328–333.

FRENZ, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution*. In *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI. Delft Univ. Press.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
MAK, T. C. W., BOOK, L., CHIEH, C., GALLAGHER, M. K., SONG, L.-C. & SEYFERTH, D. (1983). *Inorg. Chim. Acta*, **73**, 159–164.
SEYFERTH, D. & WOMACK, G. B. (1982). *J. Am. Chem. Soc.* **104**, 6839–6841.
SONG, L. C., HU, Q. M., LIU, X. Y. & WANG, J. T. (1985). *Chem. J. Chin. Univ.* **6**, 135–140.
SONG, L. C., HU, Q. M., LIU, R. G., YANG, G. Q. & WANG, J. T. (1987). *Sci. Sin. Ser. B*, **30**, 582–590.
SONG, L. C., KADIATA, M., HU, Q. M. & WANG, J. T. (1988). *Acta Chim. Sin.* **46**, 1081–1086.
SONG, L. C., KADIATA, M., WANG, J. T., WANG, R. J. & WANG, H. G. (1988). *J. Organomet. Chem.* **340**, 239–248.
SONG, L. C., LIU, J. T., LIU, R. G. & WANG, J. T. (1988). *Chem. J. Chin. Univ.* In the press.
SONG, L. C., WANG, R. J., HU, Q. M. & WANG, H. G. (1988). *Chem. J. Chin. Univ.* (*Engl. Ed.*), **4**, 38–44.
WANG, R. J., SONG, L. C., WANG, H. G. & HU, Q. M. (1987). *Jiegou Huaxue* (*J. Struct. Chem.*), **6**, 201–204.
WANG, H. G., SONG, L. C., YAO, X. K. & HU, Q. M. (1987). *J. Inorg. Chem. Chin. Chem. Soc.* **3**, 28–33.
WEI, C.-H, DAHL, L. F. (1965). *Inorg. Chem.* **4**, 1–11.
YAO, X. K., SONG, L. C., WANG, H. G., LIU, R. G., WANG, R. J. & WANG, J. T. (1987). *Acta Phys.-Chim. Sin.* **3**, 604–608.
ZHANG, J. K. (1987). Int. Conf. on the Applications of the Mössbauer Effect, August 1987, Melbourne, Australia. Abstr. P1.41.

Acta Cryst. (1989). C**45**, 579–581

The Structures of Two Permethylzirconocene Ketene Isomers: (O-*l*)- and (O-*c*)-[η^5-$C_5(CH_3)_5]_2Zr[COCHP(CH_3)_3]H$†

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Abstract. (O-*l*)-Hydridobis(η-pentamethylcyclopentadienyl)(trimethylphosphinoketene)zirconium–toluene (2/1), $C_{25}H_{41}OPZr.\frac{1}{2}C_7H_8$, $M_r = 525{\cdot}86$, monoclinic, $P2_1/n$, $a = 15{\cdot}125\,(3)$, $b = 10{\cdot}646\,(4)$, $c = 18{\cdot}306\,(4)$ Å, $\beta = 90{\cdot}168\,(25)°$, $V = 2948\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}19$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 4{\cdot}35$ cm^{-1}, $F(000) = 1116$, $T \simeq 290$ K, S (goodness-of-fit) = 4·25 (1192 reflections), $R = 0{\cdot}109$ (1108 reflections, $I > 0$), $R_{3\sigma} = 0{\cdot}086$ (847 reflections, $I > 3\sigma$). (O-*c*)-Hydridobis(η-pentamethylcyclopentadienyl)(trimethylphosphinoketene)zirconium, $C_{25}H_{41}OPZr$, $M_r = 479{\cdot}79$, monoclinic, $P2_1/c$, $a = 9{\cdot}9362\,(12)$, $b = 10{\cdot}0229\,(12)$, $c = 25{\cdot}937\,(3)$ Å, $\beta = 96{\cdot}262\,(10)°$, $V = 2567{\cdot}5\,(9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}24$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 4{\cdot}93$ cm^{-1}, $F(000) = 1016$, $T \simeq 290$ K, $S = 1{\cdot}52$ (4800), $R = 0{\cdot}042$ (4413 reflections, $I > 0$), $R_{3\sigma} = 0{\cdot}028$ (3486 reflections, $I > 3\sigma$). The cyclopentadienyl rings coordinate to Zr to form a binding pocket at the Zr atom called the equatorial wedge. In the O-*l* isomer the O atom is on a lateral coordination site (external in the equatorial wedge) while the O-*c* isomer has the O atom on the central (internal) coordination site in the equatorial wedge.

Introduction. Although the metallated ylide complex $Cp^*_2\overline{Zr(H)CH_2(PMe_2)C}H_2$ ($Me \equiv CH_3$, $Cp^* \equiv C_5Me_5$) is unreactive towards H_2 and ethylene, it does react with CO at 273 K to generate the η^2-acyl-hydride complex (*A*), (O-*l*)-$Cp^*_2Zr(COCHPMe_3)(H)$ (O-*l* ≡ oxygen lateral; Moore, 1984). If the sample is allowed to warm to room temperature, a second η^2-acyl-hydride complex (*B*), (O-*c*)-$Cp^*_2Zr(COCHPMe_3)(H)$ (O-*c* ≡ oxygen central), is found to be in equilibrium with (*A*) ($K_{eq} = 1{\cdot}58$, $A \rightleftharpoons B$ 298 K). Notable NMR and IR spectroscopic differences: ^{1}H NMR, (Zr—H̲) (*A*) δ 3·90, (*B*) δ 4·30; ν_{CO}, (*A*) 1427, (*B*) 1417 cm^{-1} (Moore, 1984). We report herein on the structures of (*A*) and (*B*).

Experimental. (O-*l*): Blue-white crystals from toluene, air-sensitive, sealed in glass capillary under N_2, 0·25 × 0·30 × 0·60 mm. Space group $P2_1/n$ by oscillation and Weissenberg photographs (systematic absences: $h0l$ for $h + l$ odd, $0k0$ for k odd). Diffractometry: Syntex $P2_1$,

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