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Synthesis and X-ray characterization of new 1-[μ-dithio-bis-(tricarbonyliron)]-2-(p-R-benzoyl)ethane complexes

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Abstract

Diiron nonacarbonyl reacts with the *para*-substituted derivatives **1a**–**d** of 3,3-dithio-1-(p-substituted phenyl)-2-propen-1-one affording surprisingly the new dinuclear Fe(0) complexes **2a**–**d** with a σ-S coordination instead of the attended η^2 or η^4 π-coordination upon the α,β-unsaturated system of the ligands. The complexes **2a**–**c** were characterized by mass spectrometry, IR and ^{1}H- and ^{13}C-NMR spectroscopies and their structures were fully confirmed by single-crystal X-ray analysis. Such structural studies revealed as the main feature an ideal C_{2v} (mm^2) symmetry with the carbonyl groups in an eclipsed configuration of the $Se_2Fe_2(CO)_6$ moiety. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Iron(0); Sulfur; Dinuclear complexes

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1. Introduction

The use and applications of ketene complexes of transition metals in organometallic chemistry as well as in organic synthesis have experienced an exponential growth in recent years [1]. Our interest in this area has centered upon the synthesis of vinylketene–Fe(0) complexes and their reactivity toward nucleophiles [2], and we have recently shown that the reaction between η^4-α,β-unsaturated ketone–Fe (CO) complexes and Me_2CuLi in absence of a CO atmosphere gave the corresponding η^4-vinylketene complexes [3].

To date most interest on this field has focused on the synthesis of novel Fe(0) complexes derived from a wide-ranging assortment of functionalized ligands. Building on the success achieved by varying the functional groups attached to α,β-unsaturated ketones, we have now extended our studies to include the dithiol group β-positioned on the α,β-unsaturated carbonylic compounds.

We thus wish to report herein our findings on the reaction of diiron nonacarbonyl with the *para*-substituted derivatives **1a**–**d** of 3,3-dithio-1-(p-substituted phenyl)-2-propen-1-one affording surprisingly the new diiron(0) complexes **2a**–**d** (Scheme 1).

2. Results and discussion

The preparation of **2a**–**d** was carried out by mixing the *para*-substituted derivatives **1a**–**d** of 2-benzoyldithioacetic acid with diiron nonacarbonyl in anhydrous diethylether under a nitrogen atmosphere during 1 h at room temperature (r.t.). After the usual workup and purification by silica-gel chromatography, the new dinuclear Fe(0) complexes were obtained.

The dinuclear 1-[μ-dithio-bis-(tricarbonyliron-(0)]-2-(p-methoxybenzoyl) ethane **2a**, a red solid obtained in a 40% yield, displayed in its IR spectrum four strong

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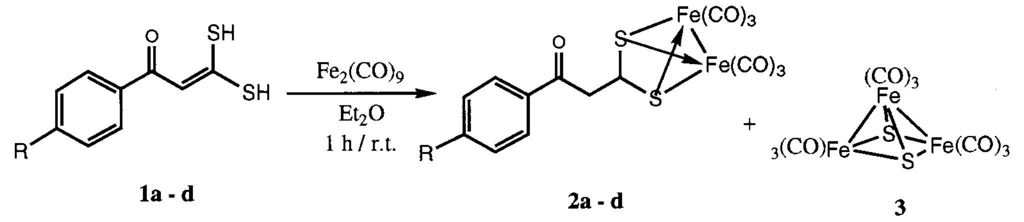


R = **a** = -OMe; **b** = -Br; **c** = -Cl; **d** = -Me

Scheme 1.

Table 1
Spectroscopic data for **2a**–**d** complexes

Compound	IR (cm^{-1})	^1H-NMR	^{13}C-NMR	MS (EI) (m/z)
2a	2068, 2037, 2015, 1990 (M–CO) 1641 (CO)	7.89, 6.96 (AA′BB′ system, 4H, $J = 9.0$ Hz, Ar); 3.9 (s, 3H, OCH_3); 5.30 (t, 1H $C\underline{H}$); 3.6 (d, 2H, $C\underline{H}_2$)	208.6, 208.3 (M–CO); 192.6 (CO); 164.2, 130.3, 128.8, 114.0 (Ar); 73.3 ($\underline{C}H$); 51.2 ($\underline{C}H_2$), 55.5 ($O\underline{C}H_3$)	450 $[M-2(CO)]^+$, 422 $[M-3(CO)]^+$, 394 $[M-4(CO)]^+$, 366 $[M-5(CO)]^+$, 338 $[M-6(CO)]^+$
2b	2081, 2034, 2005, 1971 (M–CO); 1687 (CO)	7.7, 7.6 (AA′BB′ system, 4H, $J = 8.5$ Hz, Ar); 5.30 (t, 1H, $C\underline{H}$), 3.6(d, 2H, $C\underline{H}_2$)	208.6 (M–CO); 193.1 (CO); 132.3, 129.4 (Ar); 72.7 ($\underline{C}H$); 51.4 ($\underline{C}H_2$)	555 M^+, 527 $[M-(CO)]^+$, 498 $[M-2(CO)]^+$, 470 $[M-3(CO)]^+$, 442 $[M-4(CO)]^+$, 414 $[M-5(CO)]^+$, 386 $[M-6(CO)]^+$
2c	2079, 2034, 2007, 1969, 1982 (M–CO); 1687 (CO)	7.8, 7.5 (AA′BB′ system, 4H, $J = 9$ Hz, Ar); 5.30 (t, 1H, $C\underline{H}$), 3.6 (d, 2H, $C\underline{H}_2$)	208.6 (M–CO); 193.1 (CO); 140.6, 134.1, 129.4, 129.3 (Ar); 72.7 ($\underline{C}H$); 51.4 ($\underline{C}H_2$)	510 M^+, 482 $[M-(CO)]^+$, 454 $[M-2(CO)]^+$, 426 $[M-3(CO)]^+$, 398 $[M-4(CO)]^+$, 370 $[M-5(CO)]^+$, 342 $[M-6(CO)]^+$
2d	2077, 2030, 1996, 1979 (M–CO); 1986 (CO)	7.8, 7.3 (AA′BB′ system, 4H, $J = 8$ Hz, Ar); 5.30 (t, 1H, $C\underline{H}$), 3.6 (d, 2H, $C\underline{H}_2$); 2.4 (s, 3H, CH_3)	208.6 (M–CO); 193.8 (CO); 145.0, 133.4, 129.6, 128.1 (Ar); 73.2 ($\underline{C}H$); 51.4 ($\underline{C}H_2$); 21.6 ($\underline{C}H_3$)	462 $[M-(CO)]^+$, 434 $[M-2(CO)]^+$, 406 $[M-3(CO)]^+$, 378 $[M-4(CO)]^+$, 350 $[M-5(CO)]^+$, 322 $[M-6(CO)]^+$

absorption bands in the ν(M–CO) region at 2068, 2037, 2015 and 1990 cm^{-1} and a weak intensity band assigned to an organic CO group at 1641 cm^{-1}. For this complex the ^1H-NMR spectrum revealed an AA′BB′ system at δ 7.89 and 6.96 (4H, $J = 9.0$ Hz) which fully agreed with a p-disubstituted aromatic ring. A triplet centered at δ 5.3 (1H, $J = 6.5$ Hz) attributed to the methyne bearing the sulfur atoms was coupled to a doublet at δ 3.6 (2H, $J = 6.5$ Hz) of the methylene and at δ 3.9 appeared a singlet corresponding to the methoxy group (3H). The ^{13}C-NMR spectrum showed signals at δ 208.6 and 208.3 assigned to the M–CO groups, at δ 192.6 a signal due to an organic CO group, the substituted carbon atoms showed signals at δ 164.2 and 130.3 and the rest appeared in the 128.8–114.0 range. The signals at δ 73.3 and 51.2 were assigned to the methyne and the methylene sp^3 carbons, respectively, and the methoxy group is observed at δ 55.5. The EI–MS exhibited a peak at m/z 450 owing to $[M-2CO]^+$ and the successive loss of four CO units.

On the other hand, complexes **2b**–**d** displayed very similar spectroscopic data to those obtained for **2a** (Table 1), and it must be pointed out that the synthesis of closely related dinuclear Fe(0) complexes have been reported in the literature by other methods [4,5]. It is also worthy of comment that the $S_2Fe_3(CO)_9$ complex **3** was formed (yield < 1%) in all the reactions. The complex **3** has also been obtained by other procedures [4,6,7].

The molecular structures of **2a**–**c** were fully confirmed by X-ray diffraction studies (Figs. 1–3, Table 2), and are similar to that of $CH_2S_2Fe_2(CO)_6$ [8] and also closely related to other structures possessing two $Fe(CO)_3$ fragments linked by two sulfur atoms carrying different substituents [8]. The X-ray analysis revealed that compounds **2b** and **2c** are isomorphous and there are two independent molecules in the crystal. Each molecule has an ideal C_{2v} (mm^2) symmetry with the carbonyl groups in an eclipsed configuration. The average Fe–Fe length of 2.475(11) Å is consistent with comparable distances of other complexes. Similarly, the Fe–S distances are relatively invariant (2.252–2.275 Å average 2.262 Å) and consequently the Fe–S–Fe angles cluster around the same value (range 65.9–66.5°). The S···S separation 2.675(7) Å suggests some degree of S–S interaction (non-bonding minimum separation 3.7 Å) which in turn correlates with the slight strain displayed in the S–C–S angle (mean 93.4(6)°)

The structure determination of compound **3** was carried out by an X-ray diffraction study and there is

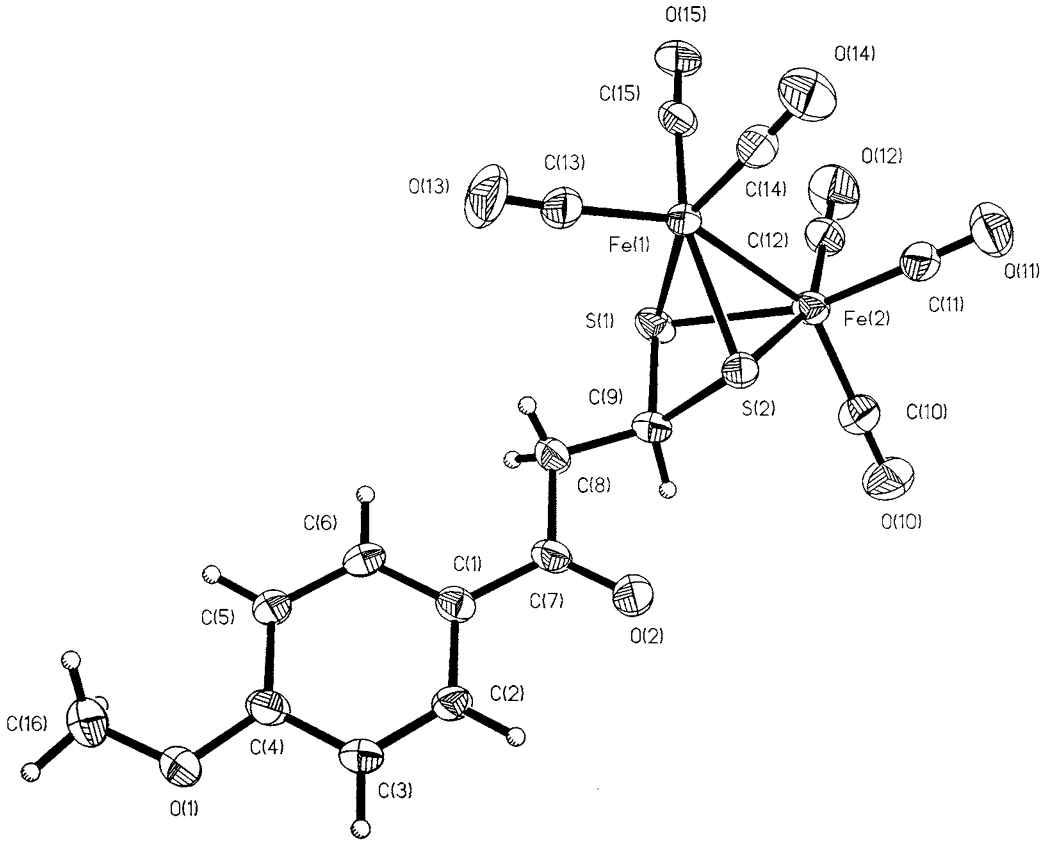


Fig. 1. The molecular structure and atom-numbers scheme for **2a**.

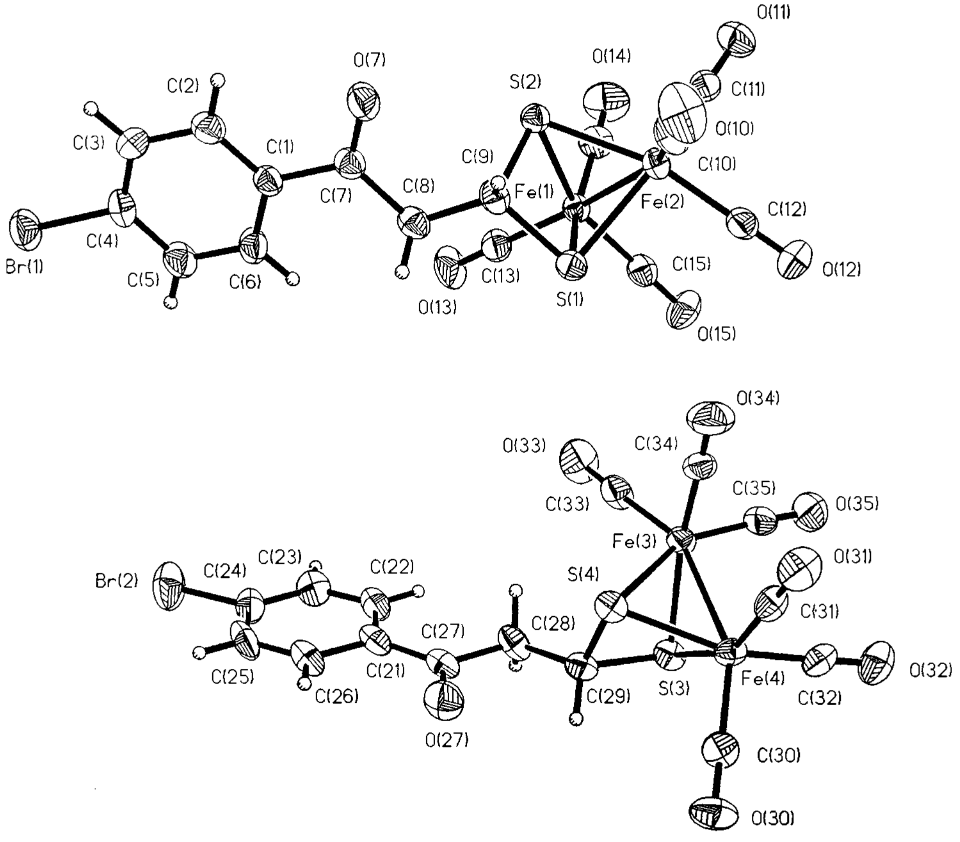


Fig. 2. The molecular structure and atom-numbers scheme for **2b**.

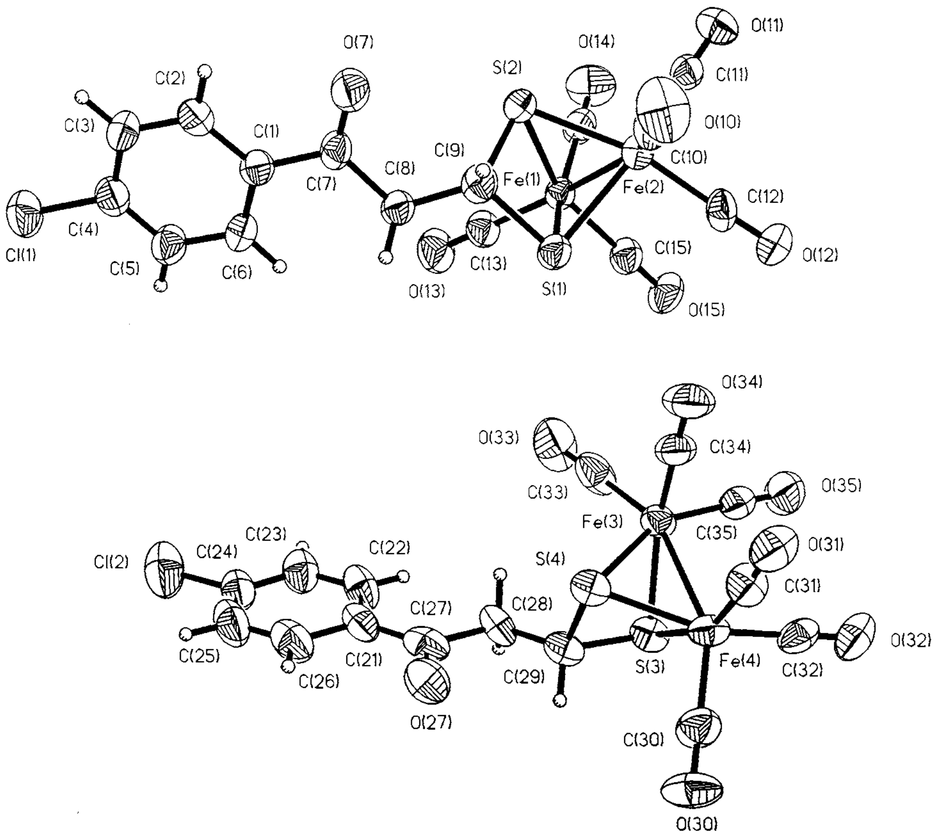


Fig. 3. The molecular structure and atom-numbers scheme for **2c**.

no essential difference in the parameters—being isomorphous with $Se_2Fe_3(CO)_9$—as reported by Dahl and Sutton [9]. Complex **3** displayed the same square pyramid framework for the heavy atoms (S and Fe) with alternated S and Fe atoms located at the corners of the basal plane and one Fe atom (hepta-coordinated) on the apex, as found by Wei and Dahl [10].

2.1. Formation of complexes *2a–d*

The formation of these complexes could be explained by a mechanism similar to that proposed by Seyferth [11]. Thus, the nucleophilic attack of the tautomeric structure **1′** upon the iron atoms of the diiron nonacarbonyl species leads to the intermediate **A**, which by loss of a CO unit gives rise to **2a–d** (Scheme 2).

Table 2
Selected bond lengths (Å) and bond angles (°)

	Compound **2a**	Compound **2b**	Compound **2c**
Fe–Fe (mean)	2.478(3)	2.477(17)	2.473(16)
Fe–S (mean)	2.267(6)	2.269(5)	2.262(6)
Fe–S–Fe (mean)	66.3(2)	66.2(3)	66.3(3)
S–Fe–S (mean)	71.9(1)	72.4(1)	72.6(2)
S–C (mean)	1.841(7)	1.840(15)	1.836(19)
S–C–S (mean)	92.6(4)	93.5(5)	93.7(9)
S···S (mean)	2.663(5)	2.679(5)	2.678(4)

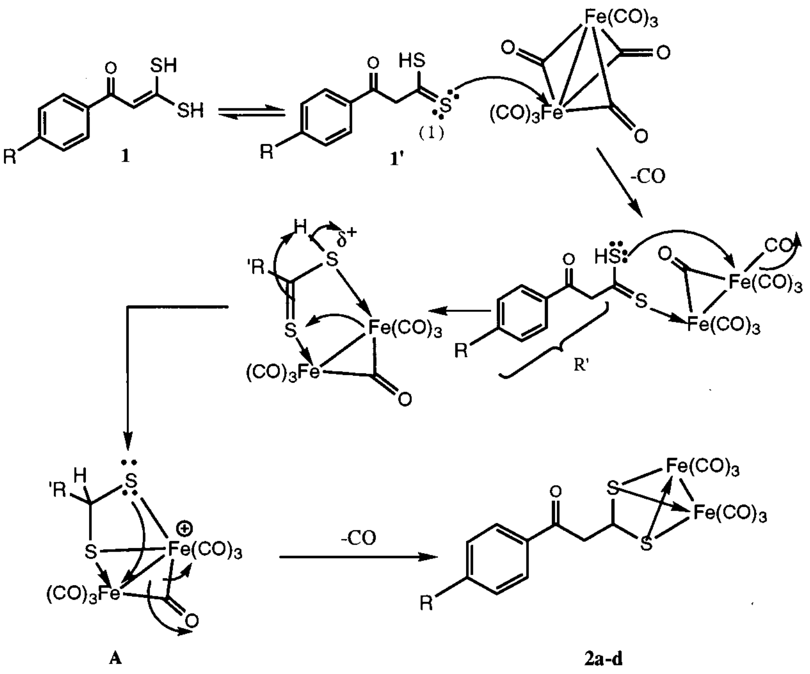
3. Conclusion

A *σ-S* coordination of the ligands **1a–d** toward $Fe_2(CO)_9$ is reported instead of the expected η^2 or η^4 π-coordination found in the case of other α,β-unsaturated carbonylic compounds, such as those of the dibenzylideneacetone [12], benzylideneacetone and chalcone–Fe(0) complexes [13]. This result could be explained by the fact that sulfur atoms may form a strong bond with the iron in a zero or low valent state in iron carbonyl complexes, according to Pearson's theory [14].

4. Experimental section

4.1. General methods

The ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian 300S spectrometer and IR spectra were recorded on a Perkin-Elmer 283 B or 1420 spectrometer. The electronic impact (EI) ionization mass spectra were acquired on a JEOL JMS-AX505 HA Mass spectrometer operated in the positive ion mode. The acquisition



Scheme 2.

Table 3
Crystal data

Compound	**2a**	**2b**	**2c**
Empirical formula	$C_{16}H_{10}Fe_2O_8S_2$	$C_{15}H_7BrFe_2O_7S_2$	$C_{15}H_7ClFe_2O_7S_2$
Formula weight	506.1	554.9	510.4
Color/shape	Red/prism	Red/prism	Red/plate
Crystal dimension		$0.64 \times 0.24 \times 0.24$	$0.60 \times 0.26 \times 0.07$
Wavelength (Å)	0.71073	0.71073	1.54178
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	8.175(2)	8.775(1)	8.708(2)
b (Å)	10.182(1)	12.988(2)	13.058(3)
c (Å)	13.401(2)	18.227(3)	18.142(4)
α (°)	73 950(1)	73.970(1)	74 400(3)
β (°)	75.620(1)	85.100(1)	84.410(3)
γ (°)	68.520(1)	77.960(1)	77.390(3)
U (Å^3)	948.0(4)	1951.8(5)	1937.3(8)
Z	2	4	4
$D_{calc.}$ (Mg m^{-3})	1.708	1.889	1.750
μ (mm^{-1})	1.726	3.781	15.622
F(000)	508	1088	1016
θ range (°)	1.50–25.00	1.50–25.00	1.50–57.50
Reflections collected	3720	7304	5682
Independent reflections (%)	3451 ($R_{int} = 2.39$)	6815 ($R_{int} = 3.94$)	5270 ($R_{int} = 4.64$)
G-O-F. on F^2	1.150	1.036	0.951
Final R indices[a]	$R = 6.47$	$R_1 = 5.47$	$R_1 = 8.24$
$[I > 2\sigma(I)]$ (%)	$wR = 11.76$	$wR_2 = 8.65$	$wR_2 = 21.02$
Parameters varied	254	487	488

[a] $R = \sum(F_o^2 - F_c^2)/\sum F_o^2$

$$wR = \left\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]\right\}^{1/2}.$$

conditions were ion source temperature 230°C, ionization energy 70 eV, emission current 0.14 μA and ionization current 100 μA. Melting points were measured using a Mel-Temp II apparatus and are uncorrected. Column chromatography was performed with Merck silica gel (70–230 mesh) using hexane/ethyl acetate in different ratios as eluent. All reagents were obtained from commercial suppliers and used as received. Reactions were performed under nitrogen atmosphere in carefully dried glassware. Diethylether was distilled from sodium-benzophenone under an argon atmosphere.

4.2. Synthesis of 1-[μ-ditio-bis-(tricarbonyliron)]-2-(p-R-benzoyl)ethane complexes

A solution of the corresponding 3,3-dimercapto-1-(*p*-substituted phenyl)-2-propen-1-one (4.4 mmol) in anhydrous diethylether was treated with $Fe_2(CO)_9$ (8.2 mmol) with stirring at r.t. for 1 h. After the reaction was complete, the solvent was evaporated under vacuum and the reaction mixture was chromatographed on silica gel. Elution with hexane/ethyl acetate in an 80/20 ratio gave the corresponding 1-[*μ*-dithio-bis-(tricarbonyliron)]-2-(*p*-*R*-benzoyl)ethane complexes and $S_2Fe_3(CO)_9$ as a byproduct in small amounts. The yield of the complexes was 40, 42, 51 and 47% for **2a**, **2b**, **2c** and **2d,** respectively, based on the pure products isolated.

4.3. X-ray data collection, structure solution and refinements for **2a–c**

Suitable crystals of complexes **2a–c** were grown by slow evaporation from a hexane:dichloromethane solution at 0°C. A summary and data collection and refinement conditions are given in Table 3. Intensities were collected on a Siemens P4/PC diffractometer using an ω-scan, those of compounds **2a** and **2b** using graphite monochromated Mo–K_α radiation and that of compound **2c** using graphite monochromatized Cu–K_α radiation. Data sets for compounds **2b**, **2c** were corrected by absorption effects. The structures were solved by direct methods and refined by full-matrix least-squares procedure [15]. Hydrogen atoms were included at idealized geometric positions and forced to ride on the carbon parent atom. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 103184, 103185, 103193 for compounds **2a–c**, respectively.

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