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Iron carbonyls with bulky thiolate ligands: crystal structures of $[Fe_2(CO)_6(\mu-SC_6H_2^{i}Pr_3-2,4,6)_2]$ and $(C_6H_2^{i}Pr_3-2,4,6)_2S_2$

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Abstract

The reaction of $Fe_3(CO)_{12}$ and bulky thiols HSR ($R = C_6H_2^{i}Pr_3-2,4,6$; $C_6H_2Me_3-2,4,6$) in toluene yielded compounds $[Fe_2(CO)_6(\mu-SR)_2]$ ($R = C_6H_2^{i}Pr_3-2,4,6$ (1), $C_6H_2Me_3-2,4,6$ (2)). The substitution of one carbonyl by the phosphine $Ph_2P(CH_2)_2Si(OEt)_3$ in complex 1 afforded $\{Fe_2(CO)_5[Ph_2P(CH_2)_2Si(OEt)_3](\mu-SC_6H_2^{i}Pr_3-2,4,6)_2\}$ (3). Mononuclear compounds $[(\eta^5-C_5H_5)Fe(CO)_2(SC_6H_2^{i}Pr_3-2,4,6)]$ (4) and $\{(\eta^5-C_5H_5)Fe(CO)[Ph_2P(CH_2)_2Si(OEt)_3](SC_6H_2^{i}Pr_3-2,4,6)\}$ (5) have also been obtained. Compound 1 has been studied by X-ray diffraction and the structure determined reveals a distorted octahedron geometry around each iron atom and confirms the anti arrangement of R substituents, $R = C_6H_2^{i}Pr_3-2,4,6$, in the molecule. The preparation of thiol HSC₆H₂ⁱPr_3-2,4,6 yielded the disulfide ($C_6H_2^{i}Pr_3-2,4,6)_2S_2$ as a by-product, whose structure has been solved by X-ray diffraction. (C) 1999 Elsevier Science S.A. All rights reserved.

Keywords: Iron complexes; Carbonyl complexes; Thiolate complexes; Crystal structures

1. Introduction

Transition metal chemistry with organosulfur ligands has played an important role in organic synthesis as well as in biological systems [1–3]. Many petroleum based hydrocarbon feedstocks contain traces of sulfur compounds, thiols among others [4–6]. From an environmental and economic point of view, studies on the hydrodesulfurisation processes are focussed on the ways to remove sulfur from the crude oil.

Compounds of formula $[Fe_2(CO)_6(SR)_2]$ as well as the phosphine derivatives $[Fe_2(CO)_{(6-n)}L_n(SR)_2]$ (n = 1, 2, or 3) are well known [7,8]. Some of them exhibit an equilibrium in solution between both *syn–anti* isomers but X-ray data have confirmed that the *anti* form is most stable in solid state. However, as far as we know, no similar compounds with sterically demanding SR ligands have been described. This type of groups has recently received attention due to its higher ability to form mononuclear compounds against the behaviour showed by the sterically less demanding thiolate ligands to bridge two metal centres. In addition, these ligands seem to facilitate the cleavage of S–C bonds, this

fact is very important from the point of view of the hydrodesulfurisation reaction [9–11] as well as in organic syntheses [3].

On the other hand, complexes containing organofunctionalised silanes have been described as adequate candidates in supported catalysis [12,13]. In this context Allum et al. [14] have studied the influence of thiols on the hydrogenation of olefins using Rh or Ir compounds with silane ligands linked to silica.

Taking into account the well-known substitution reactions of CO by phosphines as well as the hydrolysable properties of $R'_2P(CH_2)_2Si(OR)_3$ (R, R' = organic group) we wish to report here the syntheses and characterisation of some iron organometallic complexes with bulky aryl thiolate and $Ph_2P(CH_2)_2Si(OEt)_3$ ligands. X-ray data on $[Fe_2(CO)_6-(\mu-SC_6H_2^{i}Pr_3-2,4,6)_2]$ and $(C_6H_2^{i}Pr_3-2,4,6)_2S_2$ are also included.

2. Experimental

All reactions were carried out under argon atmosphere using Schlenk techniques [15]. Solvents were purified according to the standard methods [16]. The starting

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materials HSC₆H₂R₃-2,4,6 (R = ⁱPr and Me) [17], Ph₂-P(CH₂)₂Si(OEt)₃ [18], [CpFe(CO)₂I] [19], were obtained as previously described. IR spectra (2200–1600 cm⁻¹) were recorded on a Perkin-Elmer 1650 FT-IR spectrophotometer. ¹H and ³¹P{¹H} NMR were recorded on a Bruker AMX-300 spectrometer. Elemental analyses were performed on a Perkin-Elmer 240-B microanalyser. Positive ion FAB mass spectra were carried out on a WG AutoSpec spectrometer, using 3-nitrobenzyl alcohol as matrix.

2.1. $[Fe_2(CO)_6(\mu - SC_6H_2^i Pr_3 - 2, 4, 6)_2]$ (1)

Compound 1 was obtained following a modified synthesis of a previous procedure [20]. A 100 ml Schlenk flask equipped with a stirrer bar, was loaded with 1.24 g (2.46 mmol) of Fe₃(CO)₁₂ and degassed by evacuation/ argon-backfill cycles. Then 30 cm³ of toluene, and 2.85 g (12.1 mmol) of $HSC_6H_2^{i}Pr_3$ were added. The mixture was stirred for 3 h at reflux. The solvent was removed in vacuo. The resulting residue was chromatographed on silica gel 100. Elution with *n*-hexane afforded an orange band which crystallised from the concentrated hexane solution at -20° C (1.68 g, 2.24 mmol, 91% yield). Anal. Calc. for Fe₂C₃₆-H₄₆O₆S₂: C, 57.61; H, 6.18. Found: C, 57.76; H, 6.04%. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 6.93 (s, 4H, C₆H₂), 4.31 (m, 4H, o-CH(CH₃)₂), 2.82 (m, 2H, p-CH(CH₃)₂), 1.28 $(d, 24H, o-CH(CH_3)_2, J = 7 Hz), 1.20 (d, 12H, p-CH(CH_3)_2)$ J = 7 Hz). IR (cm⁻¹) (THF): ν (CO) 2069 m, 2032 vs, 2000 s, 1990 s. Mass spectrum (FAB⁺): $m/z = 750 \ (M^+)$, 694 (M^+ -2CO), 666 (M^+ -3CO), 638 (M^+ -4CO), 610 (M^+-5CO) , 582 (M^+-6CO) , 375 $(M^+-5CO-SC_6H_2^{i}Pr_3)$, 347 (M^+ -6CO-SC₆H₂ⁱPr₃).

2.2. $[Fe_2(CO)_6(\mu - SC_6H_2Me_3 - 2, 4, 6)_2]$ (2)

Using the same procedure as above with HSC₆H₂Me₃-2,4,6 (85% yield). *Anal*. Calc. for Fe₂C₂₄H₂₂O₆S₂: C, 49.51; H, 3.81. Found: C, 49.03; H, 3.88%.¹H NMR (300 MHz, CDCl₃): δ (ppm) 6.87 (s, 4H, C₆H₂), 2.60 (s, 12H, *o*-CH₃), 2.23 (s, 6H, *p*-CH₃). IR (cm⁻¹) (THF): ν (CO) 2071 m, 2035 vs, 1996 s. Mass spectrum (FAB⁺): *m*/*z* = 582 (*M*⁺), 567 (*M*⁺-CH₃), 554 (*M*⁺-CO), 526 (*M*⁺-2CO), 470 (*M*⁺-4CO), 442 (*M*⁺-5CO), 431 (*M*⁺-SC₆H₂Me₃), 414 (*M*⁺-6CO).

2.3. { $Fe_2(CO)_5[Ph_2P(CH_2)_2Si(OEt)_3](\mu-SC_6H_2^iPr_3-2,4,6)_2$ } (3)

To a solution of $[Fe_2(CO)_6(\mu-SC_6H_2^{i}Pr_3-2,4,6)_2]$ (0.17 g, 0.23 mmol) in THF (25 cm³), Ph₂P(CH₂)₂Si(OEt)₃ (0.26 g, 0.69 mmol) was added. The solution was stirred for 7 days at room temperature. The solvent was removed in vacuo and the resulting residue was chromatographed on silanised silica gel 60. Elution with toluene gave a red band of compound **3** (30% yield). *Anal.* Calc. for Fe₂C₅₅H₇₅O₈-S₂PSi: C, 60.11; H, 6.88. Found: C, 59.42; H, 6.57%. ¹H

NMR (300 MHz, CDCl₃): δ (ppm) 7.80–7.26 (m, 10H, C₆H₅), 6.87 (s, 1H, C₆H₂), 6.83 (s, 1H, C₆H₂), 4.44 (m, 2H, *o*-CH(CH₃)₂), 4.30 (m, 2H, *o*-CH(CH₃)₂), 3.65 (m, 6H, OCH₂), 2.78 (m, 2H, PCH₂), 2.58 (m, 2H, *p*-CH(CH₃)₂), 1.26 (m, 9H, OCH₂CH₃), 1.17 (m, 24H, *o*-CH(CH₃)₂), 1.12 (m, 12H, *p*-CH(CH₃)₂), 0.87 (m, 2H, CH₂Si); ³¹P{¹H} NMR (121 MHz, CDCl₃): δ (ppm) 64.7 (s, PPh₂); IR (cm⁻¹) (*n*-hexane): ν (CO) 2037 s, 1985 vs, 1967 s, 1925 m. Mass spectrum (FAB⁺): *m*/*z* = 1098 (*M*⁺), 1042 (*M*⁺-2CO), 1014 (*M*⁺-3CO), 986 (*M*⁺-4CO), 958 (*M*⁺-5CO), 723 (*M*⁺-5CO-SC₆H₂ⁱPr₃), 694 (*M*⁺-CO-Ph₂P(CH₂)₂Si(OEt)₃), 667 (*M*⁺-2CO-Ph₂P(CH₂)₂Si(OEt)₃).

2.4. $[(\eta^5 - C_5 H_5)Fe(CO)_2(SC_6 H_2^i Pr_3 - 2, 4, 6)]$ (4)

To a solution of *n*-BuLi in *n*-hexane (0.8 cm³, 1.3 mmol) at -30° C was added slowly with stirring a *n*-hexane (10 cm^3) solution of HSC₆H₂ⁱPr₃ (0.29 g, 1.23 mmol). The mixture was allowed to reach 0°C and then a THF (15 cm^3) solution of [CpFe(CO)₂I] (0.25 g, 0.8 mmol) was added. The resulting solution was stirred at room temperature for 2 h. The solvent was removed in vacuo and the residue chromatographed on silica gel 100. Elution with nhexane/THF (20:1) gave a green band. The solvent was removed and the residue recrystallised from THF/n-hexane (1:5) affording the product in 51% yield. Anal. Calc. for FeC₂₂H₂₈O₂S: C, 64.08; H, 6.84. Found: C, 63.27; H, 7.12%. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 6.84 (s, 2H, C₆H₂), 4.93 (s, 5H, C₅H₅), 4.04 (s, 2H, *o*-CH(CH₃)₂), 2.79 (s, 1H, p-CH(CH₃)₂), 1.22 (m, 18H, CH₃). IR (cm⁻ (THF): ν (CO) 2022 s, 1976 s. Mass spectrum (FAB⁺): $m/z = 412 \ (M^+), \ 356 \ (M^+ - 2\text{CO}), \ 149 \ (M^+ - \text{SC}_6\text{H}_2^{i}\text{Pr}_3 - \text{CO})$ CO).

2.5. $\{(\eta^5 - C_5 H_5)Fe(CO)[Ph_2P(CH_2)_2Si(OEt)_3](SC_6H_2^iPr_3 - 2,4,6)\}$ (5)

To a green solution of $[(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}(SC_{6}H_{2}^{i}Pr_{3}-2,4,6)]$ (0.16 g, 0.38 mmol) in CH₂Cl₂ (20 cm³), Ph₂P(CH₂)₂Si(OEt)₃ (0.15 g, 0.40 mmol) was added. After stirring for 2 h at reflux, the solvent of the brown-reddish solution was removed in vacuo and the residue recrystallised from CH₂Cl₂/*n*-hexane at $-20^{\circ}C$ (24% yield). *Anal.* Calc. for FeC₄₁H₅₇O₄SPSi: C, 64.72; H, 7.55. Found: C, 64.60; H, 7.70%. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.49–7.37 (m, 10H, C₆H₅), 6.84 (s, 2H, C₆H₂), 4.2 (s, 5H, C₅H₅), 3.97 (m, 3H, CH(CH₃)₂), 3.75 (m, 6H, OCH₂), 2.63 (t, 2H, PCH₂, *J* = 7 Hz), 1.25 (m, 9H, OCH₂CH₃), 1.20 (m, 18H, CH(CH₃)₂), 0.91 (m, 2H, CH₂Si); ³¹P{¹H} NMR (121 MHz, CDCl₃): δ (ppm) 67.4 (s, *P*Ph₂); IR/cm⁻¹ (CH₂Cl₂): ν (CO) 1937 s. Mass spectrum (FAB⁺): m/z = 760 (M^+), 732 (M^+ -CO), 667 (M^+ -CO-Cp), 497 (M^+ -CO-SC₆H₂ⁱPr₃), 356 (M^+ -CO-Ph₂P(CH₂)₂Si(OEt)₃).

Table 1 Crystallographic data

	1	6
Empirical formula	C ₃₆ H ₄₆ Fe ₂ O ₆ S ₂	C ₃₀ H ₄₆ S ₂
Fw	750.55	470.79
Crystal colour and habit	elongated prism	elongated prism
Crystal dimension (mm)	$0.17 \times 0.19 \times 0.50$	$0.17 \times 0.19 \times 0.24$
Crystal system	monoclinic	orthorhombic
Lattice parameters:		
a (Å)	10.771(1)	17.589(1)
b (Å)	27.81(1)	15.671(3)
<i>c</i> (Å)	13.639(2)	22.119(2)
α (°)	90	90
β (°)	110.33(1)	90
V (Å ³)	3831(1)	6096.8(1)
Space group	P2 ₁ /a	Pbca
$D_{\text{calc.}}$ (Mg m ⁻³)	1.301	1.026
Ζ	4	8
Radiation	Mo K α (λ =0.7107 Å)	Cu Ka (1.5407 Å)
$\mu \text{ (mm}^{-1})$	0.906	1.662
$2\theta_{\max}$ (°)	25	60
Reflections collected	6648	4538
Independent reflections	5300 $(I > 2\sigma(I))$	3027 $(I > 2\sigma(I))$
No. of parameters	415	290
Residuals R ; R_w	0.106; 0.270	0.981, 0.2428
Goodness of fit	1.191	1.048
Largest differential	0.659	0.557
peak (e Å ⁻³)		

2.6. $(C_6H_2^i Pr_3 - 2, 4, 6)_2 S_2$ (6)

Compound **6** was obtained in the preparation of $HSC_6H_2^{i}Pr_3$ -2,4,6 ligand [17]. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 6.92 (s, 4H, C₆H₂); 3.52 (m, 4H, *o*-CH(CH₃)₂); 2.82 (m, 2H, *p*-CH(CH₃)₂); 1.20 (d, 12H, *p*-CH(CH₃)₂); 1.00 (d, 24H, *o*-CH(CH₃)₂).

2.7. Crystal data for complex 1

The X-ray measurements for 1 were carried out on a PW 1100 diffractometer at room temperature, using graphite monochromated Mo Ka radiation (0.7107 Å). Relevant crystallographic data are listed in Table 1. θ Range for data collection: $2-25^{\circ}$, index ranges: $0 \le h \le 12, 0 \le k \le 33, -15$ $\leq l \leq 15$. Scattering factors, dispersion corrections and absorption coefficients were taken from the International Tables for Crystallography [21]. The structure was solved by direct methods using SIR92 [22], and was refined by least squares analysis using SHELX93 [23,24], with anisotropic thermal parameters for non-H atoms. The positions of the hydrogen atoms were refined with distance restraints for the C-H distances. No extinction correction was applied. Absorption was corrected using Ψ -scan data [25], 1.104 and 0.727, being the maximum and minimum absorption corrections. Final R indices R1 = 0.083, wR2 = 0.249 (for observed data), R indices R1: 0.106, wR2 = 0.270 (for all data), largest differential peak and hole 0.659 and -0.670 $e Å^{-3}$.

2.8. Crystal data for complex 6

The X-ray measurements for 6 were carried out on a CAD4 Enraf-Nonius diffractometer at room temperature, using graphite monochromated Cu K α radiation (1.5407 Å). Selected crystallographic data are listed in Table 1. θ Range for data collection: $4-60^{\circ}$, index ranges: $0 \le h \le 19, 0 \le k$ $\leq 17, 0 \leq 1 \leq 24$. Scattering factors, dispersion corrections and absorption coefficients were taken from the International Tables for Crystallography [21]. The structure was solved by direct methods using SIR92 [22], and was refined by least squares analysis using SHELX93 [23,24] with anisotropic thermal parameters for non-H atoms. The positions of the hydrogen atoms were refined with distance restraints for the C-H distances. The extinction correction was carried out using SHELX93 [23,24], the extinction factor being 0.0012 (2). Final R indices R1 = 0.0765, wR2 = 0.2056 (for observed data), R indices R1: 0.981, wR2 = 0.2428 (for all data), largest differential peak and hole 0.557 and $-0.393 \text{ e} \text{ Å}^{-3}$.

3. Results and discussion

Examples of $[Fe_2(CO)_6(\mu-SR)_2]$ and $[Fe_2(CO)_5(PPh_3)(\mu-SR)_2]$ derivatives are well known, however, the number of them with bulky organic group are scarce [26,27]. On the other hand, highly demanding aromatic thiolate ligands seem to show a different behaviour such as a lower tendency to bridge two metal centres when compared with the less hindered ones.

Taking into account these facts initially we carried out the reactions between $Fe_3(CO)_{12}$ and HSR ($R = C_6H_2{}^iPr_3-2,4,6$ or $C_6H_2Me_3-2,4,6$) in order to compare the results with those previously observed for alkyl or not-demanding aryl thiols.

The new complexes were characterised by elemental analysis as well as by IR, ¹H, ³¹P NMR and FAB mass spectroscopy (see Section 2). The analytical data of compounds **1** and **2** are in agreement with the formula $[Fe_2(CO)_6(\mu-SR)_2]$ ($R = C_6H_2^{\ i}Pr_3$ -2,4,6, $C_6H_2Me_3$ -2,4,6). The $\nu(CO)$ IR pattern in THF solution of both complexes is similar to those found for other related derivatives [28,29]. The ¹H NMR spectra at room temperature reveal the presence of organic groups present in the aromatic rings of both compounds. The proposed structures of **1** and **2** on the basis of analytical and spectroscopic data were confirmed by X-ray diffraction on **1** (Fig. 1).

The species $Ph_2P(CH_2)_2Si(OEt)_3$ like a phosphine may coordinate to metallic centres through the phosphorous atom. On the other hand, the presence of a hydrolysable group such as OEt in it, should facilitate the attachment of the complex to a support like silica. The importance from an industrial point of view, of supported organometallic compounds prompted us to carry out the reaction between $[Fe_2(CO)_6(\mu-SC_6H_2^{i}Pr_3-2,4,6)_2]$ and $Ph_2P(CH_2)_2Si(OEt)_3$



Fig. 1. ORTEP (50% ellipsoids) plot of compound 1.

in order to prepare {Fe₂(CO)₅[Ph₂P(CH₂)₂Si(OEt)₃](µ- $SC_6H_2^{1}Pr_3-2,4,6_2$ as reagent for the syntheses of supported catalyst. Such as has been observed in analogous compounds [Fe₂(CO)₅(PPh₃)(µ-SEt)₂] [30,31] and [Fe₂(CO)₄- $(PPh_3)_2(\mu$ -SPh)₂] [32,33], etc., the four bands displayed in the carbonyl region of the IR spectrum of 3 are indicative of the substitution of one carbonyl by one phosphine ligand from complex 2. In ³¹P NMR a resonance at 66.4 ppm has been reported for [Fe₂(CO)₅(PPh₃)(µ-SEt)₂] appearing at 44.7 ppm for $[Fe_2(CO)_4(PPh_3)_2(\mu-SEt)_2]$ [31]. Because of the free triphenylphosphine shows a resonance in ³¹P NMR quite close to that observed for the free Ph₂P(CH₂)₂-Si(OEt)₃, we believe that the signal at 64.7 ppm exhibited for 3 is in agreement with the monosubstitution. Although the reaction was carried out using an excess of phosphine, no disubstituted derivative was observed, may be due to the presence of bulky ligands in the molecule. The resonances corresponding to the organic groups of thiolate and phosphine ligands are displayed in the ¹H NMR spectrum. In the positive FAB mass spectra of 1-3 the molecular ion signal, although weak, as well as gradual loss of CO, SR or phosphine group are observed.

Reaction between $[(\eta^5-C_5H_5)Fe(CO)_2I]$ and $LiSC_6-H_2{}^iPr_3-2,4,6$ in THF afforded compound **4**. The substitution of one carbonyl by Ph₂P(CH₂)₂Si(OEt)₃ in compound **4** was carried out in refluxing THF giving compound **5**. Satisfactory elemental analyses according to the formula $[(\eta^5-C_5H_5)Fe(CO)_2(SC_6H_2{}^iPr_3-2,4,6)]$ (**4**) and $\{(\eta^5-C_5H_5)Fe(CO)_2(SC_6H_2{}^iPr_3-2,4,6)\}$ (**5**) were obtained. In the IR spectra, the bands exhibited at 2022 and 1976 cm⁻¹ for **4** and 1973 cm⁻¹ for **5** were in agreement with those found in similar compounds [34–37].

The ¹H NMR spectra of both compounds consist of several signals corresponding to the cyclopentadienyl and thiolate ligands; in addition compound **5** exhibits the resonance characteristics of the phosphine. In this case a signal at 67.4 ppm was observed in the ³¹P NMR spectrum. The molecular ion signal, in addition to the fragments corre-

sponding to loss of carbonyls, thiol or phosphine ligands were showed in the FAB mass spectrum of both complexes.

Finally, formation of the disulfide $(C_6H_2^{i}Pr_3-2,4,6)_2S_2$, as a by-product, is observed following the method previously described by Blower et al. [17] for the synthesis of $HSC_6H_2^{i}Pr_3-2,4,6$. Crystallisation in CH_2Cl_2 at $-20^{\circ}C$ gave diffraction-quality crystals of $(C_6H_2^{i}Pr_3-2,4,6)_2S_2$ (6) which could be easily separated from the mixture. This compound was characterised by ¹H NMR and its structure confirmed by X-ray diffraction.

Tai	hl	e	2

Selected bond distances (Å) and angles (°) for compounds 1 and 6

1		6	
Fe(1)–Fe(2)	2.466(2)	S(1)–S(2)	2.060(3)
Fe(1) - S(1)	2.321(2)	S(1)-C(1)	1.787(3)
Fe(1)–S(2)	2.311(2)	S(2)-C(16)	1.783(3)
Fe(2)–S(1)	2.319(2)	C(1)-S(1)-S(2)	104.5(1)
Fe(2)–S(2)	2.318(2)	S(1)-S(2)-C(16)	102.8(1)
S(2)–Fe(1)–S(1)	74.46(7)		
S(2)-Fe(2)-S(1)	74.37(7)		
Fe(2)-S(1)-Fe(1)	64.22(6)		
Fe(1)-S(2)-Fe(2)	64.40(6)		



Fig. 2. ORTEP (50% ellipsoids) plot of compound 6.



Fig. 3. PLUTO diagram showing the molecular packing of 6 projected on the **ab** plane. Holes along **c** are occupied by faced S-bridges belonging to the neighbour molecules.

3.1. Crystal structure of $[Fe_2(CO)_6(\mu-SC_6H_2^{i}Pr_3-2,4,6)_2]$ (1)

The ORTEP representation of compound **1** is shown in Fig. 1 [38]. Selected bond lengths and angles are given in Table 2. The compound shows a Fe–Fe bond almost symmetrically double bridged by two thiolate ligands with the organic group *anti* to each other. The Fe–Fe bond distance of 2.466(2) Å is shorter than that reported for similar derivatives, for instance [Fe₂(CO)₆(μ -SEt)₂] (2.537(10) Å) [39], [Fe₂(CO)₅(PPh₃)(μ -SEt)₂] (2.524(9) Å) [30,31] and [Fe₂(CO)₆(μ -SPh)₂] (2.516 Å) [40]. In **1** each iron atom is surrounded by three carbonyls and two sulfurs at the corner of a distorted octahedron. The individual Fe–C–O angles do not deviate significantly from linearity and Fe–S distances fit well with the value observed in related complexes [30,31,41,42].

3.2. Crystal structure of $(C_6H_2^i Pr_3 - 2, 4, 6)_2S_2$ (6)

Selected bond distances and angles are listed in Table 2 and a drawing of the molecule structure showing the atomnumbering scheme is given in Fig. 2 [38]. Crystals are built up of discrete molecules showing a sulfur–sulfur bridge between the 2,4,6-isopropyl trisubstituted aromatic rings. There is one crystallographically independent molecule stacked in such a way by forming holes, in which S–S bridges are situated. The mentioned holes are parallel to the *c*-axis, and each molecule is located with its S–S pair facing to another S-bridge of a neighbour molecule as shown in Fig. 3 [43]. The S–S bond distance of 2.060 (3) Å agrees well with the values observed in related compounds: $(C_6H_5)_2S_2$ (2.030 Å) [44,45], $(C_6F_5)_2S_2$ (2.059 Å), [42] and $[C_6H_2(CF_3)_3]_2S_2$ (2.053 Å) [46].

The torsion angle of 77.5° formed by the two sulfur atoms and their respective closest neighbours C₁ and C₁₆, is similar to the values found for the above mentioned compounds.

4. Supplementary material

A complete description of the crystallographic methods and details of the structure determination and refinement are available from the authors on request.

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