Sulfinyl-controlled Formation of Diastereoisomerically Pure Tricarbonyl(oxadiene)iron(0) Complexes and a Diastereoisomerically Pure Tetracarbonyl(alkene)iron(0) Complex

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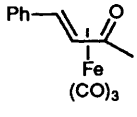
The sulfonyl and sulfinyl substituted oxadienes [RS(O)$_n$CH=CHC(Me)=O; R = Bu^t, Ph; n = 2,1] form stable tricarbonyliron(0) complexes. The sulfinyl complexes formed are diastereoisomerically pure and the relative stereochemistry of the tricarbonyliron(0) unit and the sulfinyl substituent in the products has been determined by an X-ray crystal structure analysis of [Fe^0\{Bu^{t}S(O)CH=CHC(Me)=O\}(CO)$_3$] **15a**. Phenylsulfonylethene and phenylsulfinylethene form stable tetracarbonyliron(0) complexes. The complex formed from phenylsulfinylethene is diastereoisomerically pure and the relative stereochemistry of the tetracarbonyliron(0) unit and the sulfinyl substituent has been determined by an X-ray crystal structure analysis of [Fe^0\{PhS(O)CH=CH$_2$\}(CO)$_4$] **18**. This reveals evidence for a through-space interaction between the oxygen atom of the sulfinyl substituent and the carbon atom of one of the metal carbonyl ligands. The X-ray crystal structure analysis of [Fe$_2$(μ-CH=CH$_2$)(μ-SPh)(CO)$_6$] **17**, a by-product in the formation of complex **18**, is also reported.

We are currently studying the reactivity and applications of tricarbonyliron(0) complexes of vinyl ketones. Our investigations have revealed that these complexes undergo several interesting reactions,[1,2] and that they may be converted into *inter alia* tricarbonyliron(0) complexes of vinylketenes,[3,4] vinylketenimines[5,4] and vinylallenes,[6] which, in turn, possess diverse and novel reactivity. Almost all of our exploratory work has been based on tricarbonyliron(0) complexes of α,β-unsaturated ketones with a β-phenyl substituent, a class of complex which may be exemplified by compound **1**. This is a reflection of the much greater stability of complexes of ligands bearing β-aryl substituents compared to complexes bearing β-alkyl substituents. These latter complexes may be synthesised and used, but in order to obtain acceptable yields from reactions involving them, extreme care must be taken to exclude air during all manipulations.



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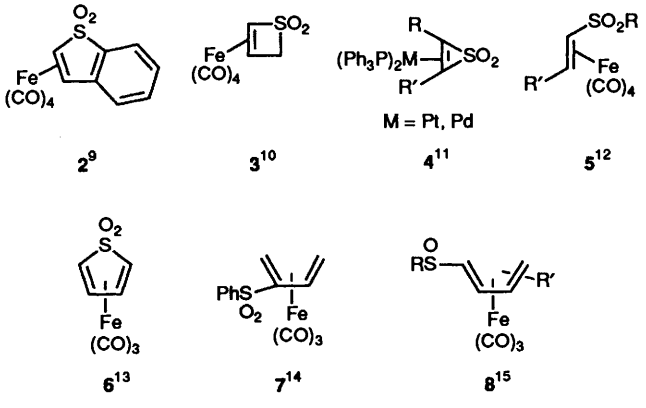
As part of a study designed to determine whether or not substituents other than aryl groups would confer stability on tricarbonyliron(0) complexes of vinyl ketones, it was decided to examine the effect on complex stability of replacing the phenyl group of **1** with sulfonyl and sulfinyl groups. It was expected that if these complexes could be synthesised, then (i) their sulfonyl and sulfinyl substituents would bestow further versatility on tricarbonyl(vinylketone)iron(0) complexes and their derivatives, and (ii) the chirality of the sulfinyl substituent would perhaps ultimately provide an entry into optically pure systems.

In recent years there has been widespread interest in the use of sulfonyl and sulfinyl substituents to control the chemical and stereochemical outcome of organic reactions.[7] In particular, the unique stereochemical properties of the sulfinyl group have attracted many organic chemists and numerous methods for exploiting its chirality have been developed.[8] It is thus surprising that there are only a few isolated examples of sulfonyl- and sulfinyl-substituted organic ligands π-bound to organometallic centres (exemplified by compounds **2**–**8**,[9–15]) and that, as far as



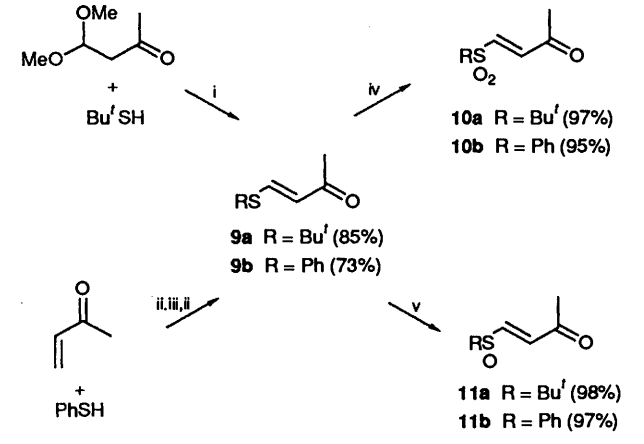
we are aware, the stereochemical effect of the sulfinyl group on organometallic complex formation has not been addressed. [The sulfinyl-substituted complexes **8** were synthesised in order to characterise the precursor dienes which had been generated by a novel method. Neither complexes **8**, nor the complexation reaction {which used [Fe(CO)$_5$] as the source of the tricarbonyliron(0) unit} are described in detail, and unfortunately the ratios of diastereoisomers formed are not presented.]

We describe, herein, experiments which demonstrate that (i) sulfonyl- and sulfinyl-substituted vinyl ketones do form very stable tricarbonyliron(0) complexes if appropriate complexation conditions are used, (ii) sulfonyl-substituted vinyl ketone complexes are precursors to stable sulfonyl-substituted vinylketene complexes, and (iii) the chirality of a sulfinyl substituent

on both vinyl ketones and alkenes exerts good stereochemical control over the formation of their respective iron carbonyl complexes. Part of this work has been the subject of a preliminary publication.[16]

Results and Discussion

Tricarbonyl(oxadiene)iron(0) *Complexes.*—Vinyl ketones substituted at their β-carbon atom with *tert*-butylsulfonyl, phenylsulfonyl, *tert*-butylsulfinyl and phenylsulfinyl groups were synthesised *via* the appropriate β-sulfenyl vinyl ketones. The β-sulfenyl vinyl ketone, 4-(*tert*-butylsulfenyl)but-3-en-2-one **9a**, was readily synthesised in good yield from acetylacetaldehyde dimethyl acetal and 1,1-dimethylethanethiol in the presence of trifluoroacetic acid using a literature procedure.[17]

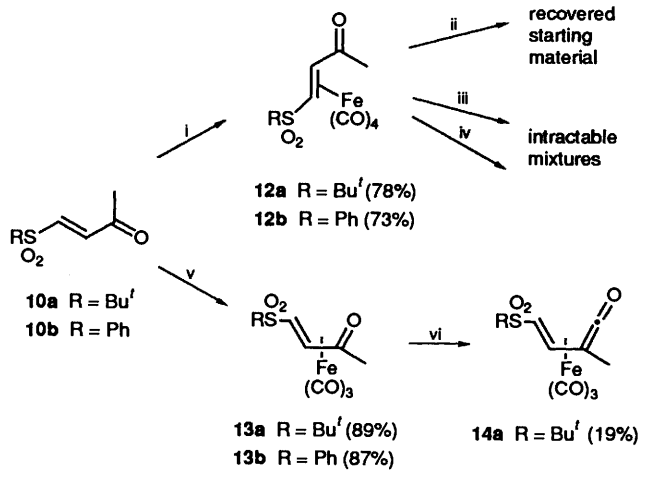


Reagents: i, CF_3CO_2H; ii, Et_3N; iii, *N*-chlorosuccinimide; iv, 2.2 equiv. *m*CPBA; v, 1.0 equiv. *m*CPBA.

The closely related β-sulfenyl substituted vinyl ketone, 4-(phenylsulfenyl)but-3-en-2-one **9b**, was also readily formed by a literature procedure.[17] Base-promoted conjugate addition of thiophenol to methyl vinyl ketone and subsequent radical chlorination and elimination of HCl gave **9b** in good yield. Oxidation of **9a** and **9b** with 2.2 equiv. of 98% *m*-chloroperbenzoic acid (*m*CPBA) proceeded very smoothly to give the known β-sulfonyl derivatives 4-(*tert*-butylsulfonyl)but-3-en-2-one **10a**[17] and (4-phenylsulfonyl)but-3-en-2-one **10b**,[17] and oxidation of **9a** and **9b** with 1.0 equiv. of 98% *m*CPBA gave the novel β-sulfinyl derivative 4-(*tert*-butylsulfinyl)but-3-en-2-one **11a**) and the previously reported β-sulfinyl derivative (4-phenylsulfinyl)but-3-en-2-one **11b**[18] in high yield.

The formation of iron carbonyl complexes from the β-sulfonyl and β-sulfinyl vinyl ketones was then addressed. The β-sulfonyl vinylketone **10a** was treated with $[Fe_2(CO)_9]$ following a procedure used previously to form **1** and related tricarbonyl(vinylketone)iron(0) complexes from the appropriate vinyl ketones in high yield.[4] A mixture of the vinyl ketone **10a** and $[Fe_2(CO)_9]$ was stirred in diethyl ether at 35 °C for 14 h. Filtration of the resulting black mixture through a short plug of alumina to remove iron residues and concentration under reduced pressure gave a yellow solid which was chromatographed and crystallised to give yellow crystals. These were identified as the novel tetracarbonyliron(0) complex **12a** on the basis of their spectral (IR, ^{1}H NMR, ^{13}C NMR, MS) and microanalytical data. Similarly, treating the β-sulfonyl vinyl ketone **10b** with $Fe_2(CO)_9$ under the same conditions gave the tetracarbonyliron(0) complex **12b** in good yield. {Complex **12b** has previously been synthesised (see general structure **5** in previous section) by treating the vinyl ketone **10b** and $[Fe_2(CO)_9]$ in benzene at 40 °C.[12]}

Decarbonylation of the tetracarbonyliron(0) complexes **12a**



Reagents: i, $[Fe_2(CO)_9]$; ii, heat; iii, Me_3NO; iv, *hv*; v, 1.1 equiv. **1**; vi, MeLi, CO

and **12b** was subsequently investigated in order to produce the desired tricarbonyliron(0) complexes of β-sulfonyl vinyl ketones. Repeated attempts to decarbonylate complexes **12a** and **12b** by thermolysis (toluene, 60 °C, 14 h; recovery of starting material), by chemical decarbonylation using Me_3NO, (1.1 equiv., acetone, 0 °C–room temp., 0.5 h; complex mixture of products) and by photolysis (toluene, room temp., 14 h; intractable black mixture) were all unsuccessful and led to either recovered starting material or intractable product mixtures as indicated.

Frustrated by the difficulties encountered in decarbonylating the tetracarbonyliron(0) complexes **12a** and **12b**, we reasoned that use of a source of the required tricarbonyliron(0) unit in the complexation step may provide a more successful route to the target tricarbonyliron(0) complexes of β-sulfonyl vinyl ketones. Thus, the sulfones **10a** and **10b** were stirred with 1.1 equiv. of tricarbonyl(benzylideneacetone)iron(0) **1** at 35 °C for 14 h in a solvent mixture of pentane and toluene (1 : 1). Chromatography of the two product mixtures (to remove benzylideneacetone) and crystallisation produced two sets of orange–yellow crystals which were identified as the new tricarbonyliron(0) complexes **13a** and **13b** on the basis of their spectral (IR, ^{1}H, ^{13}C, MS) and microanalytical data. Gratifyingly complexes **13a** and **13b** proved to be completely air-stable in the solid state and only very slightly air-sensitive in solution. Thus they are as stable and as easy to manipulate as complex **1** and other tricarbonyliron(0) complexes of β-phenyl α,β-unsaturated ketones.

The complexation procedure used in the successful approach to sulfonyl complexes **13a** and **13b** is worthy of further comment. Transfer of the tricarbonyliron(0) unit from complex **1** to hydrocarbon dienes is well documented,[19] but as far as we are aware, the reactions described above are the first examples of transfer of the tricarbonyliron(0) unit from one vinyl ketone to a second vinyl ketone. It is of note that the transfer of the tricarbonyliron(0) unit from complex **1** to sulfones **10a** and **10b** at 35 °C over 14 h is relatively efficient (yields of 89 and 87% respectively), as transfer of the tricarbonyliron(0) unit from benzylideneacetone to hydrocarbon dienes is usually a little less efficient (typically yields are 60–70%) and requires higher reaction temperatures (typically 60–90 °C) and longer reaction times (typically 24–48 h).

Tricarbonyl[4-(*tert*-butylsulfonyl)but-3-en-2-one]iron(0) **13a** was converted into tricarbonyl[5(*tert*-butylsulfonyl)-3-methyl-1-oxapenta-1,2,4-triene)iron(0) **14a** using a procedure previously reported for complex **1** and its analogues. Complex **13a** was stirred with methyllithium in tetrahydrofuran at −78 °C under a carbon monoxide atmosphere for 1 h. After being warmed to room temperature and stirred for a further 2 h,

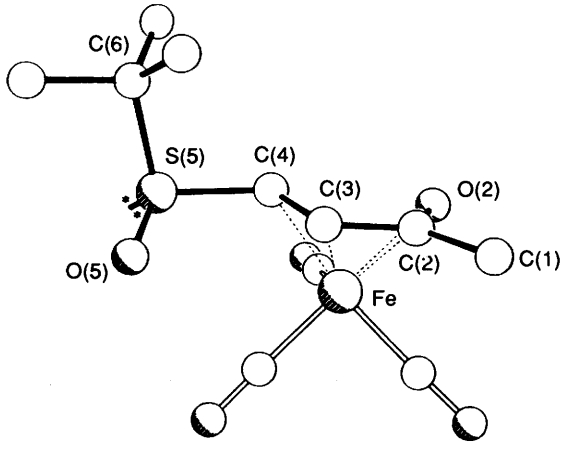


Fig. 1 Molecular structure of $[Fe^0\{Bu^tS(O)CH{=}CHC(Me){=}O\}(CO)_3]$ **15a**. Selected bond lengths (Å), bond angles and torsion angles (°): C(1)–C(2) 1.490(5), C(2)–C(3) 1.406(6), C(3)–C(4) 1.421(4), C(4)–S(5) 1.772(4), S(5)–C(6) 1.844(5), C(2)–O(2) 1.312(5), S(5)–O(5) 1.500(3), Fe–O(2) 2.024(3), Fe–C(2) 2.097(5), Fe–C(3) 2.054(5), Fe–C(4) 2.073(4); O(2)–C(2)–C(3) 115.2(3), C(2)–C(3)–C(4) 115.7(3), C(3)–C(4)–S(5) 118.8(3), C(4)–S(5)–C(6) 100.4(2), C(4)–S(5)–O(5) 106.2(2), O(5)–S(5)–C(6) 106.4(2), O(2)–C(2)–C(3)–C(4) 5.3(6), C(2)–C(3)–C(4)–S(5) −174.0(3), C(3)–C(4)–S(5)–C(6) −95.4(4), C(3)–C(4)–S(5)–O(5) 15.2(4).

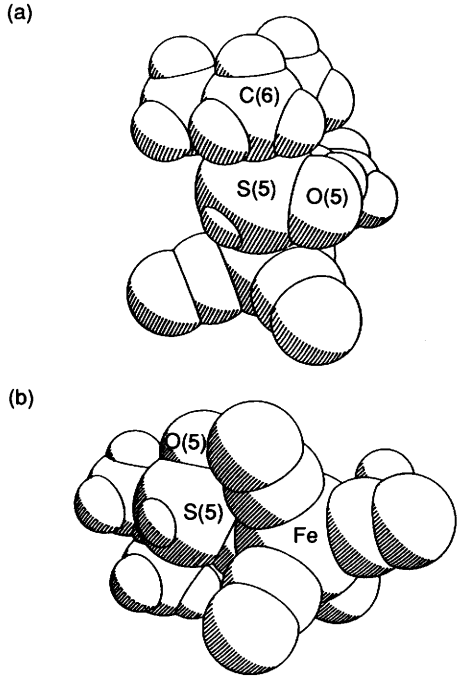
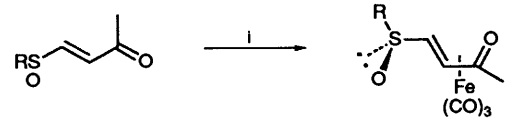


Fig. 2 Space filling model of $[Fe^0\{Bu^tS(O)CH{=}CHC(Me){=}O\}(CO)_3]$ **15a** viewed (a) down the S(5)–C(4) bond, and (b) through the $Fe(CO)_3$ tripod towards the vinylketone ligand

the resulting dark brown mixture was chromatographed and crystallised. This gave yellow crystals which were identified as complex **14a** on the basis of their spectral (IR, ^{1}H NMR, ^{13}C NMR, MS) and microanalytical data. The rather disappointing yield obtained for this reaction probably reflects alkyllithium attack on the sulfonyl substituent of **13a**.

Attention then turned to the complexation of the sulfoxides 4-(*tert*-butylsulfinyl)but-3-en-2-one **11a** and 4-(phenylsulfinyl)-but-3-en-2-one **11b**. Complexation of the sulfoxides **11a** and **11b** was examined under conditions identical with those used for the successful complexation of the sulfones **10a** and **10b**. Accordingly, the sulfoxide **11a** was stirred with 1.1 equiv. of tricarbonyl(benzylideneacetone)iron(0) **1** at 35 °C for 14 h in a solvent mixture of pentane and toluene (1:1). Filtration of the product mixture through a short plug of alumina to remove iron residues and subsequent solvent evaporation gave a red oil which was examined by 270 MHz ^{1}H NMR spectroscopy. This revealed that the red oil contained benzylideneacetone, a new complex and tricarbonyl(benzylideneacetone)iron(0) **1** in a ratio of 65:27:8. Column chromatography on silica led to the isolation of each of these components plus a minor fourth component which contained no protons. This minor component of the product mixture was tentatively assigned as a mixture of clusters containing iron atoms, sulfur atoms and carbonyl groups.[20,21] The yellow band containing the new complex was evaporated to dryness, examined by 270 MHz ^{1}H NMR spectroscopy and then crystallised from pentane. The crystalline air-stable complex was fully characterised and identified as a single diastereoisomer of tricarbonyl(4-*tert*-butylsulfinyl)but-3-en-2-one)iron(0) **15a** produced in 35% yield. Careful examination of the 270 MHz ^{1}H NMR spectra of the crude product and of complex **15a** prior to crystallisation indicated that only one diastereoisomer had been present in the product mixture. Similarly, when 4-(phenylsulfinyl)but-3-en-2-one **11b** was subjected to identical reaction conditions, work-up, and analysis, the novel diastereoisomerically pure complex **15b** was isolated in 32% yield. Examination of the data obtained again revealed that only one diastereoisomer of the sulfinyl complex was



11a R = Bu^t **15a** R = Bu^t (67%)
11b R = Ph **15b** R = Ph (64%)

Reagents: i, 1.4 equiv. **1**

present in the product mixture and that the crude reaction product contained benzylideneacetone, complex **15b** and complex **1** in a ratio of 6:2:1. Subsequent optimised complexation reactions of **11a** and **11b** using 1.4 equiv. of complex **1** gave diastereoisomerically pure **15a** and **15b** in 67 and 64% yield respectively.

The relative stereochemistry of the single diastereoisomer of **15a** produced by transfer of the tricarbonyliron(0) unit from the benzylideneacetone complex **1** to the sulfoxide **11a** was determined by an X-ray crystal structure analysis (Fig. 1). This revealed that in the diastereoisomer formed, the oxygen of the sulfinyl group is placed surprisingly close to a metal carbonyl ligand whilst the sterically less demanding sulfinyl lone pair lies between two metal carbonyl ligands (Fig. 2). It was noted at this point that in contrast to the single resonance normally associated with the three fluxional carbonyl ligands in tricarbonyl(diene)iron(0) complexes at room temperature,[22] the room temperature ^{13}C NMR spectra of sulfinyl complexes **15a** and **15b** and the sulfonyl complexes **13a** and **13b** each contained three sharp signals corresponding to the metal-carbonyl carbons, thus revealing that in solution at room temperature interchange of the three metal carbonyl groups in these complexes is restricted.

Tetracarbonyl(alkene)iron(0) Complexes.—The stability of the sulfonyl-substituted complexes **12a**, **12b**, **13a** and **13b**, and the stability and interesting stereochemical properties of sulfinyl-substituted complexes **15a** and **15b** led us to examine the synthesis and properties of iron carbonyl complexes of commercially available phenylsulfonylethene and phenylsulfinylethene. We were particularly interested in the stereochemical outcome of complexation of phenylsulfinylethene, and whether or not its sulfinyl substituent would control the relative stereochemistry

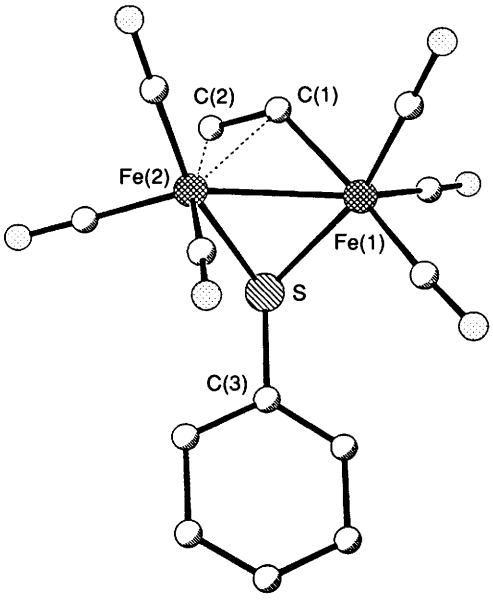
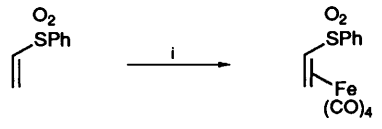


Fig. 3 Molecular structure of $[Fe_2(\mu\text{-}CHCH_2)(\mu\text{-}SPh)(CO)_6]$ **17**. Selected bond lengths (Å) and bond angles (°): Fe(1)–Fe(2) 2.545(1), Fe(1)–C(1) 1.966(4), Fe(2)–C(1) 2.076(4), Fe(2)–C(2) 2.182(5), C(1)–C(2) 1.367(6), Fe(1)–S 2.262(1), Fe(2)–S 2.275(1), S–C(3) 1.793(4); Fe(1)–S–Fe(2) 68.3(1), Fe(1)–C(1)–C(2) 128.0(3).

of the complex formed, as had been observed with complexes **15a** and **15b**.

Initially, phenylsulfonylethene was stirred with $[Fe_2(CO)_9]$ in diethyl ether at 35 °C for 14 h. Subsequent work-up and crystallisation led to the production of a very stable pale yellow crystalline material which was identified as the tetracarbonyl complex **16**. The novel complex, formed in excellent yield (92%), was fully characterised.



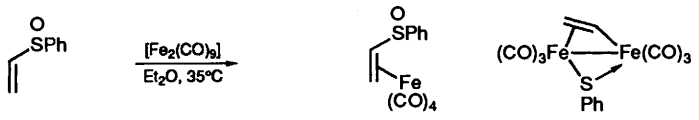
16 (92%)

Reagents: i, $[Fe_2(CO)_9]$

Attention then turned to the formation of an iron carbonyl complex from phenylsulfinylethene. In the first experiment performed, phenylsulfinylethene was stirred with $[Fe_2(CO)_9]$ in diethyl ether at 35 °C for 21 h. Column chromatography of the reaction mixture led to the development of three major bands. [Inital elution with 60–80 °C light petroleum–diethyl ether, 4:1, gave a red band followed by a more polar yellow band. Subsequent rechromatography of the red band using light petroleum (b.p. 30–40 °C) followed by light petroleum (b.p. 60–80 °C) gave two red bands]. Collection, evaporation to dryness and crystallisation of the *less polar* red band gave a red crystalline solid which was identified by X-ray crystallography as the dimetallic complex **17** (Fig. 3). {Complex **17** has previously been synthesised by treating $[Et_3NH][Fe_2(\mu\text{-}CO)(\mu\text{-}C_6H_5S)(CO)_6]$ with vinylmercuric bromide,[23] and related complexes in which the phenyl group is replaced by alkyl and vinyl groups have been synthesised by stirring the appropriate sulfenylethenes with $[Fe_3(CO)_{12}]$.[24]} Collection and evaporation to dryness of the second *more polar* red band gave considerable quantities of a red oil which was tentatively assigned as a mixture of clusters containing at least iron carbonyl ligands (eight strong absorptions in the IR spectrum in the range 2074–1965 cm^{-1}) and phenyl groups (a multiplet in the range δ 7.1–7.4 was the only signal observed in the ^1H NMR spectrum). Collection, evaporation to dryness and crystallisation of the yellow band gave a yellow crystalline solid which was identified and fully characterised as the novel complex tetracarbonyl(phenylsulfinylethene)iron(0) **18**. Although we were delighted to observe that this material was diastereoisomerically pure, the yield of complex **18** from this reaction was somewhat disappointing (28%). Thus the reaction was repeated but this time it was only allowed to proceed for 3.25 h. Analysis of the crude product mixture by ^1H NMR spectroscopy (270 MHz) showed that it contained the required tetracarbonyl complex **18** and the di-iron complex **17** in a 55:2 ratio. A relatively small multiplet at δ 7.1–7.4 indicated the presence of small amounts of the material previously tentatively assigned as clusters containing iron carbonyl and phenyl groups. The spectrum was examined closely for signals which could be assigned to the minor diastereoisomer of complex **18** and, indeed, very small signals at δ 2.76 and 4.55 may be attributed to the minor diastereoisomer. The ratio of the resonances due to the major diastereoisomer to these resonances was 55:1. Subsequent column chromatography of the crude product mixture led to the isolation of diastereoisomerically pure tetracarbonyl(phenylsulfinylethene)-iron(0) in 55% yield.

Complex **18** was examined by X-ray crystallography in order to determine the relative stereochemistry of the sulfinyl substituent and the iron carbonyl unit. The resulting structure is depicted in Figs. 4 and 5. It is worthy of comment that in complex **18** there is good evidence for a through-space interaction between the oxygen atom of the sulfinyl group [O(2)] and the carbon atom of one of the iron carbonyl ligands [C(4)]. The distance between the two atoms was found to be 2.76 Å (considerably less than the sum of their van der Waals radii, which is approximately 3.1 Å). Furthermore, the carbonyl group with which the sulfinyl oxygen appears to be interacting is significantly more bent than the three other metal carbonyl ligands. The Fe–C(4)–O(1) bond angle was found to be 170.4(4)° whilst the three remaining carbonyl ligands were found to have Fe–C–O angles of 178.5(3), 178.4(4) and 177.8(4)°. Re-examination of the structure of complex **15a** revealed that the distance between its sulfinyl oxygen and the carbon atom of the closest metal carbonyl ligand was 3.12 Å and that the Fe–C–O bond angle of the same metal carbonyl was 177.8(5)°. [The remaining two metal carbonyl ligands have Fe–C–O bond angles of 178.2(5) and 179.3(5)°.] Thus an interaction appears unlikely in this case and the restricted interchange of the three metal carbonyl groups in complex **15a** is probably due to the bulk of the sulfur atom. However, it is possible that interactions between the sulfinyl oxygen atom of the ligand and a metal carbonyl group during the formation of **15a** may lead to the observed diastereoselectivity. Finally, it is of note that the sulfur lone pair in complex **18** is directed away from the metal centre in the diastereoisomer formed. Presumably in this orientation, interaction of the lone pair with metal orbitals leading to insertion of the iron atom into the C(2)–S bond and ultimately the formation of products such as complex **17** is prevented.

In conclusion, we have demonstrated that iron carbonyl complexes of sulfonyl-substituted ligands are extremely stable and formed in very high yield. More significantly, our results indicate that the chirality of sulfinyl substituents has a considerable stereochemical effect on the formation of iron carbonyl complexes. Investigations of the effect of sulfinyl substituents in several other transition metal systems are currently being undertaken in order to (*a*) determine whether or not this effect is general or merely confined to iron complexes, and (*b*) understand the origin of the effect.



	18	17	Fe-CO and Ph containing clusters	candidate for second diastereoisomer of sulfoxide complex
For time = 21 h, isolated yields:	28%	10%	considerable quantity	
For time = 3.25 h, ratio in crude product:	55	2	very small amount	1
and isolated yield:	55%			

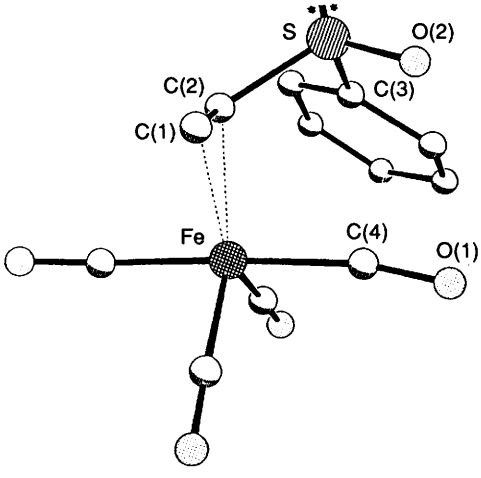


Fig. 4 Molecular structure of $[Fe^0\{PhS(O)CH{=}CH_2\}(CO)_4]$ **18**. Selected bond lengths (Å) and bond angles (°). Fe–C(1) 2.069(3), Fe–C(2) 2.058(3), C(1)–C(2) 1.407(5), C(2)–S 1.812(4), S–O(2) 1.508(3), S–C(3) 1.771(3); C(1)–C(2)–S 117.6(3), C(2)–S–O(2) 108.9(2), C(2)–S–C(3) 99.0(2), C(3)–S–O(2) 106.9(1), Fe–C(4)–O(1) 170.4(4).

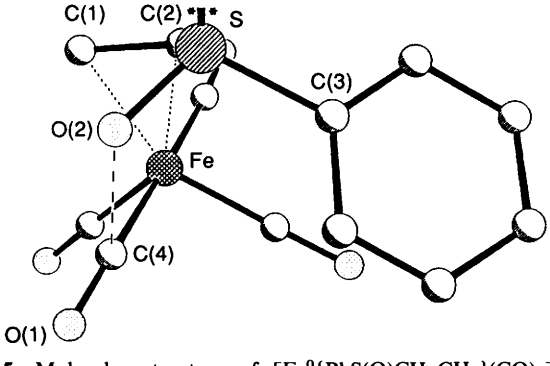


Fig. 5 Molecular structure of $[Fe^0\{PhS(O)CH{=}CH_2\}(CO)_4]$ **18** viewed down the S-C(2) bond. O(2)–C(4) = 2.76 Å (see Results and Discussion)

Experimental

Reactions under nitrogen and carbon monoxide were performed using standard vacuum line and Schlenk tube techniques.[25] Tetrahydrofuran was distilled from sodium benzophenone ketyl. Diethyl ether was dried over Na wire. Dichloromethane was distilled from P_2O_5. Light petroleum (b.p. 40–60 °C) was distilled. $[Fe_2(CO)_9]$,[26] 4-(*tert*-butylsulfenyl)but-3-en-2-one **9a**,[17] 4-(phenylsulfenyl)but-3-en-2-one **9b**,[17] and tricarbonyl(benzylideneacetone)iron(0) **1**[4] were prepared using literature procedures. The concentration of MeLi was determined by titration against diphenylacetic acid.[27] Commercially available *m*CPBA (50–60%) was purified as described below. All other reagents were used as obtained from commercial sources. M.p.s were obtained on a Reichert 7905 hot-stage microscope and a Gallenkamp capillary m.p. apparatus and are uncorrected. The m.p.s of organoiron complexes were measured in sealed capillaries under nitrogen. Elemental analyses were performed by MEDAC Ltd, Brunel University Chemistry Department and Imperial College Microanalytical Service. IR spectra were obtained on a Perkin-Elmer 1710 FTIR instrument. NMR spectra were recorded in $CDCl_3$ (unless stated otherwise) at room temperature on Perkin–Elmer R34 (220 MHz ^1H) and Bruker WH 400 (400 MHz ^1H, 100.6 MHz ^{13}C) spectrometers at Warwick University and JEOL GSX 270 (270 MHz ^1H, 67.9 MHz ^{13}C) and Bruker AM 500 (125.8 MHz ^{13}C) spectrometers at Imperial College. Mass spectra were recorded on a Kratos MS 80 instrument at Warwick University, on VG Mass Lab 12/250 and VG Analytical ZAB/E instruments at the SERC Mass Spectrometry Service Centre, Swansea, and on a VG Micromass 7070E instrument at Imperial College using EI, CI and FAB (matrix—*m*-nitrobenzylalcohol[28]) techniques. The X-ray crystal structure of tricarbonyl(4-(*tert*-butylsulfinyl)but-3-en-2-one)iron(0) **15a** has been reported previously.[16] Atomic coordinates bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Purification of 50–60% m*CPBA*.[29]—A pH 7.5 buffer solution was prepared by mixing aqueous $Na_2HPO_4{\cdot}12H_2O$ (71.64 g dm^{-3}, 0.2 mol dm^{-3}; 42 cm^3) and aqueous $NaH_2PO_4{\cdot}2H_2O$ (31.21 g dm^{-3}, 0.2 mol dm^{-3}; 8 cm^3). *m*CPBA (50–60%; 5.2 g) was dissolved in diethyl ether (100 cm^3) and washed with the buffer described above (6 × 50 cm^3), water (2 × 50 cm^3) and saturated brine (2 × 50 cm^3). The diethyl ether layer was dried ($MgSO_4$), filtered and evaporated to give *m*CPBA (2.68 g) which was shown to be 98% pure by thiosulfate/iodine titration.

4-(tert-*Butylsulfonyl*)*but*-3-*en*-2-*one* **10a**.—4-(*tert*-Butylsulfenyl)but-3-en-2-one **9a** (1.185 g, 7.5 mmol) was dissolved in dichloromethane (50 cm^3) and cooled to 0 °C. To this rapidly stirred solution, a solution of *m*CPBA (2.850 g, 16.0 mmol) in dichloromethane (15 cm^3) was added dropwise over 15 min. The reaction mixture was stirred at 0 °C for 2 h, allowed to warm to room temperature, and then stirred for a further 2 h. The resulting white slurry was then washed with 10% aqueous NaOH (4 × 30 cm^3), water (3 × 30 cm^3) and brine (3 × 30 cm^3). The organic phase was dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a white waxy solid. Crystallisation of this from diethyl ether–pentane produced the title compound **10a**[17] as white needles (1.380 g, 97%), m.p. 113–116 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1709s, 1694s (C=O), 1309s and 1117s (SO_2); δ_H(220 MHz) 1.4 [9 H, s, $C(CH_3)_3$], 2.4 (3 H, s, $COCH_3$), 7.15 (1 H, d, *J* 15, $Bu^tSO_2CH{=}CHCOMe$) and 7.25 (1 H, d, *J* 15, $Bu^tSO_2CH{=}CHCOMe$); $\delta_C\{^1H\}$(125.8 MHz) 23.1 [$C(CH_3)_3$], 29.5 ($COCH_3$), 59.1 [$C(CH_3)_3$], 135.0 ($Bu^tSO_2CH{=}CHCOMe$), 140.3 ($Bu^tSO_2CH{=}CHCOMe$) and 195.1 ($COCH_3$); *m*/*z* (CI, NH_3) 208 (M^+ + 18, 100%).

4-(*Phenylsulfonyl*)*but*-3-*en*-2-*one* **10b**.—4-(Phenylsulfenyl)-but-3-en-2-one **9b** (1.000 g, 5.6 mmol) was dissolved in

dichloromethane (100 cm^3) and the solution cooled to 0 °C. To this rapidly stirred solution, a solution of *m*CPBA (2.130 g, 12.3 mmol) in dichloromethane (30 cm^3) was added dropwise over 15 min. The reaction mixture was stirred at 0 °C for 2 h, allowed to warm to room temperature, and then stirred for a further 2 h. The resulting white slurry was then washed with 10% aqueous NaOH (4 × 30 cm^3), water (3 × 30 cm^3) and brine (3 × 30 cm^3). The organic phase was dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a white waxy solid. Crystallisation of this from diethyl ether–pentane produced 4-(phenylsulfonyl)but-3-en-2-one **10b**[17] as white needles (1.110 g, 95%), m.p. 62–64 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1710s, 1693s (C=O), 1327s and 1152s (SO_2); δ_H(400 MHz) 2.36 (3 H, s, $COCH_3$), 7.02 (1 H, d, *J* 15.4, $PhSO_2CH$=C*H*COMe) and 7.16 (1 H, d, *J* 15.4, $PhSO_2$C*H*=CHCOMe), 7.6 (2 H, t, *J* 7, H_{meta}), 7.7 (1 H, t, *J* 7, H_{para}) and 7.9 (2 H, *J* 7, H_{ortho}); $\delta_C\{^1H\}$(125.8 MHz) 29.1 (CO*C*H_3), 128.2 and 129.6 (C_{ortho} and C_{meta}), 134.4 and 136.0 ($PhSO_2CH$=*C*HCOMe and C_{para}), 138.4 (C_{ipso}), 140.9 ($PhSO_2$*C*H=CHCOMe) and 195.5 (*C*OCH_3); *m/z* (CI, NH_3) 228 (M^+ + 18, 100%) and 101 (C_4H_5OS, 66).

4-(tert-*Butylsulfinyl*)*but*-3-*en*-2-*one* **11a**.—4-(*tert*-Butylsulfenyl)but-3-en-2-one **9a** (1.975 g, 12.5 mmol) was dissolved in dichloromethane (50 cm^3) and the solution cooled to 0 °C. To this rapidly stirred solution, a solution of *m*CPBA (2.160 g, 12.5 mmol) in dichloromethane (15 cm^3) was added dropwise over 15 min. The reaction mixture was stirred at 0 °C for 2 h, allowed to warm to room temperature, and then stirred for a further 2 h. The resultant white slurry was then washed with 10% aqueous NaOH (4 × 30 cm^3), water (3 × 30 cm^3) and brine (3 × 30 cm^3). The organic phase was dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a white waxy solid. Crystallisation of this from diethyl ether–pentane produced the *title compound* **11a** as white needle crystals (2.130 g, 98%), m.p. 41.5–43 °C (Found: C, 55.2; H, 8.0; $C_8H_{14}O_2S$ requires C, 55.14; H, 8.10%); ν_{max}(hexane)/cm^{-1} 1704s (C=O) and 1077s (SO); δ_H(400 MHz) 1.20 [C(CH_3)$_3$], 2.27 (3 H, s, $COCH_3$), 6.81 (1 H, d, *J* 15.0, Bu^{t}SOCH=C*H*COMe) and 7.36 (1 H, d, *J* 15.0, Bu^{t}SOC*H*=CHCOMe); $\delta_C\{^1H\}$(100.6 MHz) 23.1 [C(*C*H_3)$_3$], 29.2 [CO(*C*H_3)$_3$], 56.8 [*C*(CH_3)$_3$], 134.0 (Bu^{t}SOCH=*C*HCOMe), 144.1 (Bu^{t}SO*C*H=CHCOMe) and 194.2 (*C*OCH_3); *m/z* (CI, NH_3) 192 (M^+ + 18, 12%), 175 (M^+ + 1, 54) and 101 (C_4H_5OS, 100).

4-(*Phenylsulfinyl*)*but*-3-*en*-2-*one* **11b**.—4-(Phenylsulfenyl)-but-3-en-2-one **9b** (1.620 g, 9.1 mmol) was dissolved in dichloromethane (100 cm^3) and the solution cooled to 0 °C. To this rapidly stirred solution, a solution of *m*CPBA (1.570 g, 9.1 mmol) in dichloromethane (30 cm^3) was added dropwise over 15 min. The reaction mixture was stirred at 0 °C for 2 h, allowed to warm to room temperature, and then stirred for a further 2 h. The resulting white slurry was then washed with 10% aqueous NaOH (4 × 30 cm^3), water (3 × 30 cm^3) and brine (3 × 30 cm^3). The organic phase was dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a white waxy solid. Crystallisation from diethyl ether–pentane produced the title compound[18] **11b** as white needles (1.710 g, 97%), m.p. 72–74 °C; ν_{max}(hexane)/cm^{-1} 1714s (C=O) and 1086m (SO); δ_H(400 MHz) 2.32 (3 H, s, $COCH_3$), 6.95 (1 H, d, *J* 15.0, PhSOCH=C*H*COMe) and 7.32 (1 H, d, *J* 15.0, PhSOC*H*=CHCOMe), 7.50–7.54 (3 H, m, H_{meta} and H_{para}) and 7.59–7.62 (2 H, m, H_{ortho}); $\delta_C\{^1H\}$(100.6 MHz) 29.1 ($COCH_3$), 124.6 and 129.7 (C_{ortho} and C_{meta}), 130.2 and 131.7 (PhSOCH=*C*HCOMe and C_{para}), 141.5 (C_{ipso}), 149.2 (PhSO*C*H=CHCOMe) and 194.7 (*C*OCH_3); *m/z* (CI, NH_3) 195 (100, M^+ + 1).

Tetracarbonyl[4-(tert-*butylsulfonyl*)*but*-3-*en*-2-*one*]*iron*(0) **12a**.—A mixture of 4-(*tert*-butylsulfonyl)but-3-en-2-one **10a** (0.120 g, 0.63 mmol) and [$Fe_2(CO)_9$] (0.50 g, 1.37 mmol) was stirred in diethyl ether (7 cm^3) under nitrogen at 35 °C for 14 h. Filtration of the resulting black mixture through a short plug of alumina with diethyl ether gave a yellow solution which was concentrated under reduced pressure to give a yellow solid. Column chromatography (SiO_2; ethyl acetate–light petroleum, 1:3) gave yellow crystals which were recrystallised from hexane to give the *title compound* **12a** as yellow needles (0.177 g, 78%), m.p. 106–108 °C (decomp.) (Found: C, 40.1; H, 4.2. $C_{12}H_{14}FeO_7S$ requires C, 40.24; H, 3.94%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2120s, 2100m, 2050vs, 2020vs (C≡O) 1740vw, 1640w (C=O), 1290m and 1120 m (SO_2); δ_H(220 MHz) 1.45 [9 H, s, C(CH_3)$_3$], 2.35 (3 H, s, $COCH_3$), 3.55 (1 H, d, *J* 10, Bu^tSO_2CH=C*H*COMe) and 4.3 (1 H, d, *J* 10, Bu^tSO_2C*H*=CHCOMe); $\delta_C\{^1H\}$(100.6 MHz) 24.0 [C(*C*H_3)$_3$], 29.2 ($COCH_3$), 49.5 (Bu^tSO_2CH=*C*HCOMe), 55.2 (Bu^tSO_2*C*H=CHCOMe), 59.8 [*C*(CH_3)$_3$] and 202.8 (*C*OCH_3); *m/z* (CI, NH_3) 359 (M^+ + 1, 14%), 331 (MH − CO, 8), 208 [M − $Fe(CO)_4$ + NH_4, 29)] and 57 (Bu^t, 100).

Tetracarbonyl[4-(*phenylsulfonyl*)*but*-3-*en*-2-*one*]*iron*(0) **12b**.—A mixture of 4-(phenylsulfonyl)but-3-en-2-one **10b** (0.115 g, 0.55 mmol) and [$Fe_2(CO)_9$] (0.438 g, 1.20 mmol) was stirred in diethyl ether (7 cm^3) under nitrogen at 35 °C for 14 h. Filtration of the resulting black mixture through a short plug of alumina with diethyl ether gave a yellow solution which was concentrated under reduced pressure to give a yellow solid. Column chromatography (SiO_2; ethyl acetate–light petroleum, 1:3) of the latter gave yellow crystals which were recrystallised from hexane to give the title compound **12b**[12] as yellow needles (0.151 g, 73%), m.p. 96–98 °C (decomp.); $\nu_{max}(CHCl_3)/cm^{-1}$ 2117s, 2094w, 2055vs, 2022vs (C≡O), 1730vw, 1674w (C=O), 1300w and 1130w (SO_2); δ_H(270 MHz) 2.31 (3 H, s, $COCH_3$), 3.66 (1 H, d, *J* 9.6, $PhSO_2CH$=C*H*COMe), 4.37 (1 H, d, *J* 9.6, $PhSO_2$C*H*=CHOMe), 7.52–7.62 (3 H, m, H_{meta} and H_{para}) and 7.91–7.93 (2 H, m, H_{ortho}); $\delta_C\{^1H\}$(100.6 MHz) 29.4 (CO*C*H_3), 47.2 ($PhSO_2CH$=*C*HCOMe), 64.7 ($PhSO_2$*C*H=CHCOMe), 127.1, 129.5 (C_{ortho} and C_{meta}), 133.3 (C_{para}), 141.2 (C_{ipso}), 202.3br (C=O), 203.1 (*C*OCH_3), 203.7br and 205.2br (C≡O); *m/z* (CI, NH_3) 396 (M^+ + NH_4, 4%), 379 (MH, 3), 228 [M − $Fe(CO)_4$ + NH_4, 31] and 179 [M − $Fe(CO)_4$ − 2O + H, 100].

Tricarbonyl[4-(tert-*butylsulfonyl*)*but*-3-*en*-2-*one*]*iron*(0) **13a**.—4-(*tert*-Butylsulfonyl)but-3-en-2-one **10a** (0.095 g, 0.50 mmol) and tricarbonyl(benzylideneacetone)iron(0) **1** (0.157 g, 0.55 mmol) were stirred in a mixture of pentane and toluene (1:1; 7 cm^3) under nitrogen at 35 °C for 14 h. The resulting deep red mixture was filtered through a plug of alumina using diethyl ether as eluent. Subsequent solvent removal under reduced pressure left a red oil which after column chromatography (SiO_2; ethyl acetate–light petroleum, 2:3) and solvent removal left yellow crystals. Subsequent recrystallisation from hexane gave the *title compound* **13a** as orange–yellow needles (0.146 g, 89%), m.p. 99–101 °C (Found: C, 39.9; H, 4.3. $C_{11}H_{14}FeO_6S$ requires C, 40.02; H, 4.27); ν_{max}(hexane)/cm^{-1} 2082vs, 2025vs and 2010vs (C≡O); δ_H(220 MHz) 1.45 [9 H, s, C(CH_3)$_3$], 2.5 (3 H, s, $COCH_3$), 2.75 (1 H, d, *J* 7, Bu^tSO_2C*H*=CH) and 5.8 (1 H, d, *J* 7, Bu^tSO_2CH=C*H*); $\{^1H\}$(100.6 MHz) 20.6 (CO*C*H_3), 23.7 [C(*C*H_3)$_3$], 59.1 (Bu^tSO_2*C*H=CH), 59.4 [*C*(CH_3)$_3$], 76.2 (Bu^t-SO_2CH=*C*H), 146.2 (*C*OCH_3), 202.1, 204.4 and 206.8 (C≡O); *m/z* (EI, 70 eV, 180 °C) 330 (M^+, 1%), 302 (M − CO, 1), 274 (M − 2CO, 12), 246 (M − 3CO, 7), 190 [M − $Fe(CO)_3$, 10] and 57 (Bu^t, 100).

Tricarbonyl[4-(*phenylsulfonyl*)*but*-3-*en*-2-*one*]*iron*(0) **13b**.—4-(Phenylsulfonyl)but-3-en-2-one **10b** (0.105 g, 0.50 mmol) and tricarbonyl(benzylideneacetone)iron(0) **1** (0.157 g, 0.55 mmol) were stirred in a mixture of pentane and toluene (1:1; 7 cm^3)

under nitrogen at 35 °C for 14 h. The resulting deep red mixture was filtered through a plug of alumina using diethyl ether as eluent. Subsequent solvent removal under reduced pressure left a red oil which after column chromatography (SiO_2; ethyl acetate–light petroleum, 2:3) and solvent removal left yellow crystals. Subsequent recrystallisation from hexane gave the *title compound* **13b** as orange–yellow needles (0.150 g, 87%), m.p. 109–111 °C (Found: C, 44.5; H, 3.0. $C_{13}H_{10}FeO_6S$ requires C, 44.60; H, 2.88%); ν_{max}(hexane)/cm^{-1} 2091vs, 2035vs and 2018vs (C≡O), 1327 and 1146 (SO_2); δ_H(400 MHz) 2.43 (3 H, s, $COCH_3$), 2.72 (1 H, d, *J* 7.0, $PhSO_2CH$=CH), 5.78 (1 H, d, *J* 7.0, $PhSO_2CH$=C*H*), 7.56 (2 H, t, *J* 7, H_{meta}), 7.64 (1 H, t, *J* 7, H_{para}), 7.95 (2 H, d, *J* 7, H_{ortho}); $\delta_C\{^1H\}$(100.6 MHz) 20.5 ($COCH_3$), 67.5 ($PhSO_2CH$=CH), 73.6 ($PhSO_2CH$=*C*H), 127.0, 129.3 (C_{ortho} and C_{meta}), 133.3 (C_{para}), 141.3 (C_{ipso}) 147.6 ($COCH_3$), 201.8, 204.8 and 206.7 (C≡O); *m/z* (EI, 70 eV, 180 °C) 350 (M^+, 0.1%), 322 (M − CO, 0.1), 294 (M − 2CO, 5), 266 (M − 3CO, 4), 218 [M − $Fe(CO)_3$, 13] and 43 (CH_3CO, 100).

Tricarbonyl[5-(tert-*butylsulfonyl*)-3-*methyl*-1-*oxapenta*-1,2,4-*triene*]*iron*(0)**14a**.—Tricarbonyl[4-(*tert*-butylsulfonyl)but-3-en-2-one]iron(0) **13a** (0.260 g, 0.79 mmol) was dissolved in THF (4 cm^3) under a carbon monoxide atmosphere and the solution cooled to −78 °C. Methyllithium (0.59 cm^3, 0.87 mmol) was added dropwise and the reaction mixture was stirred at −78 °C for 1 h. The cooling bath was then removed and the reaction mixture allowed to warm to room temperature and then it was stirred for a further 2 h. The resultant dark brown mixture was filtered through alumina to remove iron residues and the solvent removed under reduced pressure to give a yellow oil. Chromatography [SiO_2; ethyl acetate:light petroleum (b.p. 40–60 °C), 2:3] and crystallisation from pentane gave the *title compound* **14a** as yellow crystals (0.050 g, 19%), m.p. 103–107 °C (decomp.) (Found: C. 41.85; H, 4.1. $C_{12}H_{14}FeO_6S$ requires C, 42.12; H, 4.12%); ν_{max}(hexane)/cm^{-1} 2087vs, 2041vs and 2013vs (C≡O) and 1797mbr (C=O); δ_H(400 MHz) 1.46 [9 H, s, $C(CH_3)_3$], 1.86 (3 H, s, 3-CH_3), 2.56 (1 H, d, *J* 7.1, CH=C*H*SO_2Bu^t) and 6.09 (1 H, d, *J* 7.1, C*H*=CHSO_2Bu^t); $\delta_C\{^1H\}$(100.6 MHz) 13.3 (3-CH_3), 23.8 [$C(CH_3)_3$], 48.1 (C-3), 54.5 (C-5), 59.8 [$C(CH_3)_3$], 100.3 (C-4), 207.2br (C≡O) and 230.9 (C-2); *m/z* (FAB) 343 (MH^+, 95%), 287 (MH^+ − 2CO, 100), 259 (MH^+ − 3CO, 83), 230 (M^+ − 4CO, 57) and 174 (M^+ − 4CO − Fe, 51).

Tricarbonyl[4-(tert-*butylsulfinyl*)*but*-3-*en*-2-*one*]*iron*(0) **15a**.—4-(*tert*-butylsulfinyl)but-3-en-2-one **11a** (0.104 g, 0.60 mmol) and tricarbonyl(benzylideneacetone)iron(0) **1** (0.188 g, 0.66 mmol) were stirred in a mixture of pentane and toluene (1:1; 7 cm^3) under nitrogen at 35 °C for 14 h. The resulting brown mixture was filtered through a plug of alumina using diethyl ether as eluent. Subsequent solvent removal under reduced pressure left a red oil which contained benzylideneacetone, complex **15a** and complex **1** (65:27:8) according to ^1H NMR spectroscopy (270 MHz). Column chromatography (SiO_2; ethyl acetate:light petroleum, 2:3) and solvent removal gave yellow crystals which contained only one diastereoisomer of complex (**15a**) (^1H NMR spectroscopy, 270 MHz, $CDCl_3$). Subsequent recrystallisation from pentane gave the *title compound* **15a** as orange–yellow needles (0.066 g, 35%), m.p. 102–104 °C (Found: C, 42.3; H, 4.6. $C_{11}H_{14}FeO_5S$ requires C, 42.01; H, 4.50); ν_{max}(hexane)/cm^{-1} 2080vs, 2091vs, 2012vs (C=O) and 1060w (S=O); δ_H(270 MHz) 1.28 [9 H, s, $C(CH_3)_3$], 2.50 (3 H, s, $COCH_3$), 2.65 (1 H, d, *J* 7.3, Bu^tSO_2CH=CH) and 5.97 (1 H, d, *J* 7.3, Bu^tSO_2CH=C*H*); δ_H(270 MHz, C_6D_6) 0.98 [9 H, s, $C(CH_3)_3$], 1.95 (3 H, s, $COCH_3$), 2.78 (1 H, d, *J* 7.3, Bu^tSO_2CH=CH) and 5.96 (1 H, d, *J* 7.3, Bu^tSO_2CH=C*H*); $\delta_C\{^1H\}$(100.6 MHz) 20.7 ($COCH_3$), 22.9 [$C(CH_3)_3$], 56.0 [$C(CH_3)_3$], 63.2 (Bu^tSO_2CH=CH), 71.8 (Bu^tSO_2CH=*C*H), 145.0 ($COCH_3$), 202.2, 205.6 and 208.8 (C≡O); δ_C(C_6H_6, 125.8 MHz) 20.2 ($COCH_3$), 22.5 [$C(CH_3)_3$], 55.3 [$C(CH_3)_3$], 65.0 (Bu^tSO_2CH=CH), 72.0 (Bu^tSO_2CH=*C*H), 146.3 ($COCH_3$), 203.3, 206.4 and 210.1 (C≡O); *m/z* (CI, NH_3) 315 (M^+ + 1, 7%), 299 (M + 1 − O, 14), 175 [M + 1 − $Fe(CO)_3$, 5] 159 (M + 1 − $Fe(CO)_3$ − O, 100) and 57 (Bu^t, 60).

Tricarbonyl[4-(*phenylsulfinyl*)*but*-3-*en*-2-*one*]*iron*(0) **15b**.—4-(Phenylsulfinyl)but-3-en-2-one **11b** (0.116 g, 0.60 mmol) and tricarbonyl(benzylideneacetone)iron(0) **1** (0.188 g, 0.66 mmol) were stirred in a mixture of pentane and toluene (1:1; 7 cm^3) under nitrogen at 35 °C for 14 h. The resulting brown mixture was filtered through a plug of alumina using diethyl ether as eluent. Subsequent solvent removal under reduced pressure left a red oil which contained benzylideneacetone, complex **11b** and complex **1** (6:2:1) according to ^1H NMR spectroscopy (270 MHz). Column chromatography (SiO_2; ethyl acetate–light petroleum, 2:3) and solvent removal gave yellow crystals which contained only one diastereoisomer of complex **11b** (^1H NMR spectroscopy, 270 MHz). Subsequent recrystallisation from pentane gave *tricarbonyl*[4-(*phenylsulfinyl*)*but*-3-*en*-2-*one*]*iron*(0) **11b** as orange–yellow needles (0.063 g, 32%), m.p. 104–106 °C (Found: C, 47.0; H, 3.0. $C_{13}H_{10}FeO_5S$ requires C, 46.73; H, 3.02); ν_{max}(hexane)/cm^{-1} 2079vs, 2012vs, 2009vs (C≡O) and 1059w (S=O); δ_H(270 MHz) 2.46 (3 H, s, $COCH_3$), 2.82 (1 H, d, *J* 7.3, $PhSO_2CH$=CH), 5.80 (1 H, d, *J* 7.3, $PhSO_2CH$=C*H*) and 7.57 (5 H, s, Ph); δ_H(270 MHz, C_6D_6) 1.72 (3 H, s, $COCH_3$), 2.68 (1 H, d, *J* 7.6, $PhSO_2CH$=CH), 5.28 (1 H, d, *J* 7.6, $PhSO_2$-CH=C*H*), and 6.96–7.28 (5 H, m, Ph); $\delta_C\{^1H\}$(100.6 MHz) 20.5 ($COCH_3$), 73.9 ($PhSO_2CH$=CH), 77.9 ($PhSO_2CH$=*C*H), 122.8, 129.3 (C_{ortho} and C_{meta}), 130.9 (C_{para}), 145.4, 146.5 (C_{ipso} and $COCH_3$), 202.1, 206.1 and 207.3 (C≡O); δ_H(C_6D_6, 67.8 MHz) 20.3 ($COCH_3$), 74.4 ($PhSO_2CH$=CH), 79.9 ($PhSO_2CH$=*C*H), 123.2, 129.68 (C_{ortho} and C_{meta}), 130.9 (C_{para}), 147.0 and 148.2 (C_{ipso} and $COCH_3$), 203.6, 207.4 and 208.7 (C≡O); *m/z* (CI, NH_3) 179 [M + 1 − $Fe(CO)_3$ − O, 100%). (The mass spectrum of complex **11b** was recorded under several conditions but in no case was a molecular ion observed.)

Tetracarbonyl(*phenylsulfonylethene*)*iron*(0) **16**.—Phenylsulfonylethene (0.300 g, 1.79 mmol) and [$Fe_2(CO)_9$] (1.41 g, 3.87 mmol) were heated together in diethyl ether (10 cm^3) at 35 °C for 14 h under nitrogen. The resulting mixture was filtered through a plug of alumina and the solvent removed under reduced pressure. Column chromatography [SiO_2; light petroleum (b.p. 40–60 °C):ethyl acetate, 3:1] of the resulting green oil yielded a pale yellow solid which was crystallised from pentane to give the *title compound* **16** as pale yellow needles (0.55 g, 92%), m.p. 92–96 °C (decomp.) (Found: C, 42.8; H, 2.7. $C_{12}H_8FeO_6S$ requires C, 42.88; H, 2.49); ν_{max}(hexane)/cm^{-1} 2107m, 2051m, 2028vs, 2008vs (C≡O), 1329m and 1152s (SO_2); δ_H(400 MHz) 2.39 (1 H, dd, *J* 8 and 3, CH=CH$H_{(E)}$), 2.59 (1 H, dd, *J* 11 and 3, CH=CH$H_{(Z)}$, 3.78 (1 H, dd, *J* 11 and 8, C*H*=CH_2), 7.54 (2 H, t, *J* 8, H_{meta}), 7.61 (1 H, t, *J* 8, H_{para}) and 7.95 (2 H, d, *J* 8, H_{ortho}); $\delta_C\{^1H\}$(100.6 MHz) 27.3 (CH=*C*H_2), 65.2 (*C*H=CH_2), 127.1, 129.2 (C_{ortho} and C_{meta}), 132.8 (C_{para}), 142.0 (C_{ipso}) and 206.2 (C≡O); *m/z* (CI, NH_3) 354 (M^+ + NH_4, 23%) and 186 [M + NH_4 − $Fe(CO)_4$, 100].

Hexacarbonyl(μ-*ethenyl*)(μ-*phenylsulfenyl*)*di-iron*(0) **17** *Tetracarbonyl*(*phenylsulfinylethene*)*iron*(0) **18**.—Phenylsulfinylethene (2.50 g, 16.4 mmol) and [$Fe_2(CO)_9$] (5.95 g, 16.4 mmol) were heated together at 35 °C in diethyl ether (100 cm^3) for 21 h under nitrogen. The resulting red mixture was passed through a plug of alumina (Brockmann 1, neutral; diethyl ether) and the solvent was evaporated to give a red oil. Column chromatography (SiO_2, Kieselgel 60) of the red oil led to the development and collection of three major bands. Initial column chromato-

Table 1 Atomic coordinates (× 10^4) per compound **17**

	x	y	z
Fe(1)	8 736(1)	−821(1)	6 669(1)
Fe(2)	7 233(1)	840(1)	7 044(1)
S(1)	7 761(1)	−1 894(1)	7 597(1)
C(1)	8 267(3)	−1 751(5)	8 661(2)
C(2)	9 098(4)	−2 689(6)	8 916(3)
C(3)	9 466(5)	−2 648(8)	9 744(4)
C(4)	8 987(7)	−1 684(10)	10 301(4)
C(5)	8 165(7)	−791(9)	10 058(4)
C(6)	7 784(5)	−807(7)	9 228(3)
C(1′)	7 525(3)	−456(6)	5 953(2)
C(2′)	6 623(3)	−1 050(7)	6 084(3)
C(7)	9 804(3)	−561(6)	7 400(3)
O(7)	10 508(2)	−386(5)	7 807(2)
C(8)	9 006(3)	−2 930(6)	6 193(3)
O(8)	9 133(3)	−4 271(5)	5 872(2)
C(9)	9 270(3)	687(6)	5 969(3)
O(9)	9 603(3)	1 653(5)	5 528(2)
C(10)	8 005(3)	2 116(6)	7 791(3)
O(10)	8 468(2)	2 941(5)	8 273(2)
C(11)	6 095(3)	848(6)	7 465(3)
O(11)	5 370(3)	808(5)	7 727(3)
C(12)	7 021(3)	2 854(6)	6 420(3)
O(12)	6 882(3)	4 134(5)	6 035(2)

Table 2 Atomic coordinates (× 10^4) per compound **18**

	x	y	z
Fe	6781(1)	304(1)	7972(1)
C(1)	7037(3)	−233(3)	9791(3)
C(2)	7028(3)	−1255(3)	9031(3)
S(2)	5818(1)	−2362(1)	8901(1)
O(3)	4659(2)	−1701(3)	8911(2)
C(3)	5655(3)	−2845(3)	7359(3)
C(4)	6587(3)	−3488(3)	7069(3)
C(5)	6446(4)	−3833(4)	5888(4)
C(6)	5375(4)	−3547(4)	4991(4)
C(7)	4431(4)	−2940(4)	5295(4)
C(8)	4560(3)	−2592(3)	6481(3)
C(10)	8438(4)	333(4)	8244(4)
O(10)	9481(3)	362(3)	8441(4)
C(20)	6578(3)	−220(3)	6422(3)
O(20)	6472(3)	−518(3)	5447(3)
C(30)	5102(3)	405(4)	7752(3)
O(30)	4083(3)	620(3)	7540(3)
C(40)	6776(3)	1952(4)	7996(3)
O(40)	6749(3)	2979(3)	7993(3)

graphy [light petroleum (b.p. 60–80 °C)–diethyl ether, 4:1] separated a less polar red band from a lower R_f yellow band. The red fraction was then further subjected to column chromatography [light petroleum (b.p. 30–40 °C) followed by light petroleum (b.p. 60–80 °C)] and this revealed two red bands. The least polar band was evaporated under reduced pressure and the resulting red oily solid was crystallised from light petroleum–diethyl ether to give hexacarbonyl(μ-ethenyl)(μ-phenylsulfenyl)di-iron(0) **17** as a red crystalline solid (0.70 g, 10%), m.p. 67–70 °C (Found: C, 40.8; H, 2.1. $C_{14}H_8Fe_2O_6S$ requires C, 40.42; H, 1.94); $\nu_{max}(CCl_4)$ 2076m, 2041vs and 2003vs (C≡O); δ_H(270 MHz) 3.05 (1 H, dd, *J* 1.95, 14.2, CH=CH$H_{(Z)}$), 3.93 (1 H, dd, *J* 1.95, 9.3, CH=CH$H_{(E)}$), 7.2–7.3 (5 N, m, Ph) and 8.24 (1 H, dd, *J* 9.3, 14.2, C*H*=CH_2); $\delta_C\{^1H\}$(125.8 MHz) 73.2 (CH=*C*H_2), 127.8 (C_{para}), 128.6, 128.8 (C_{ortho} and C_{meta}), 131.5 (C_{ipso}), 156.3 (*C*H=CH_2), 208br and 201.0 (C≡O); *m/z* (EI) 416 (M^+, 6%), 388 ($M^+ - 28 \times 1$, 6), 360 ($M^+ - 28 \times 2$, 4), 332 ($M^+ - 28 \times 3$, 1), 304 ($M^+ - 28 \times 4$, 2), 280 ($M^+ - 28 \times 5$,2), 248 ($M^+ - 28 \times 6$,19) and 136 [$M^+ - Fe_2(CO)_6$, 100]. The second more polar red band was evaporated and the resulting red oil was tentatively assigned as a mixture of clusters containing at least iron-carbonyl fragments and phenyl groups (see Results and Discussion). The yellow band was evaporated to give a yellow oil which was crystallised from light petroleum (b.p. 60–80 °C) to give *tetracarbonyl(phenylsulfinylethene)iron*(0) **18** as a yellow crystalline solid (1.45 g, 28%), m.p. 54–55 °C (Found: C, 45.2; H, 2.5. $C_{12}H_8FeO_5S$ requires C, 45.03; H, 2.52); $\nu_{max}(CCl_4)/cm^{-1}$ 2094, 2034, 2015, 1995 (C≡O) and 1057 (SO); δ_H(270 MHz) 2.48 [1 H, dd, *J* 2.9 and 7.8, CH≡CH$H_{(E)}$], 2.61 [1 H, dd, *J* 2.9 and 11.2, (CH=CH$H_{(Z)}$], 4.03 (1 H, dd, *J* 7.8 and 11.2, C*H*=CH_2) and 7.5–7.65 (5 H, m, Ph); $\delta_C\{^1H\}$(125.8 MHz) 26.9 (CH=*C*H_2), 73.6 (*C*H=CH_2), 123.4, 129.2 (C_{ortho} and C_{meta}), 130.7 (C_{para}), 147.3 (C_{ipso}), 207.6 (C≡O); *m/z* (CI) 321 (MH^+, 9%), 153 [MH − $Fe(CO)_4$, 100] and 137 [MH − $Fe(CO)_4$ − O, 87].

X-Ray Crystallographic Analysis of **17**.—*Crystal data.* Single crystals of **17**, suitable for X-ray crystallography were grown from light petroleum (b.p. 60–80 °C)–diethyl ether. $C_{14}H_8Fe_2O_6S$, M = 416.0, monoclinic, a = 13.941(3), b = 7.287(2), c = 16.152(3) Å, β = 95.79(2)°, U = 2633 Å^3, space group $P2_1/a$, Z = 4, D_c = 1.69 g cm^{-3}. Red, air stable prisms dimensions 0.43 × 0.60 × 0.70 mm, μ(Mo-Kα) = 19.3 cm^{-1}, F(000) = 832. 2879 Independent measured reflections were collected on a Siemens P4/PC diffractometer, ω-scan method, ($3 \leqslant 2\theta \leqslant 50°$), graphite monochromated Mo-Kα radiation (λ = 0.710 73 Å) with 2191 observed [$|F_o| > 3\sigma(|F_o|)$] and corrected for Lorentz and polarisation factors. No absorption factor was applied. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. The hydrogen atoms on C(1′) and C(2′) were located from a ΔF map and refined isotropically subject to a distance constraint (C–H = 0.96 Å). All the other hydrogen atoms were idealised (C–H = 0.96 Å), assigned isotropic thermal parameters, U(H) = 0.08 and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares to give R = 0.037, R_w = 0.041 ($w^{-1} = \sigma^2(F) + 0.001\,41F^2$). The maximum residual electron density in the final ΔF map was 0.35 e Å^{-3} and the mean and maximum shift/error in the final refinement cycle were 0.010 and 0.046 respectively. Computations were carried out on an IBM PS/2386 using the SHELXTL PC program system.[30] Atomic co-ordinates for non-hydrogen atoms are given in Table 1. Bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

X-Ray Crystallographic Analysis of **18**.—*Crystal data.* Single crystals of **18** suitable for X-ray crystallography were grown from light petroleum (b.p. 60–80 °C). $C_{12}H_8FeO_5S$, M = 320.1, monoclinic, a = 11.377(3), b = 10.967(3), c = 11.230(2) Å, β = 105.70(2)°, U = 1348.9 Å^3, space group $P2_1/a$, Z = 4, D_c = 1.58 g cm^{-3}. Yellow air-stable prisms, dimensions 0.45 × 0.65 × 0.73 mm, μ(Mo-Kα) = 12.8 cm^{-1}, F(000) = 648. 2375 Independent measure reflections were collected on a Siemens P4/PC diffractometer ω-scan method, ($3 \leqslant 2\theta \leqslant 50°$), graphite monochromated Mo-Kα radiation (λ = 0.710 73 A) with 1980 observed [$|F_o| > 3\sigma(|F_o|)$] and corrected for Lorentz and polarisation factors. No absorption corrections were applied. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. The thermal parameters of the hydrogen atoms on C(1) and C(2) were allowed to refine isotropically. All the other hydrogen atoms were idealised (C–H = 0.96 Å), assigned isotropic thermal parameters, U(H) = 0.08 and allowed to ride on their parent carbons. Refinement was by full-matrix least squares to give R = 0.043, R_w = 0.048 ($w^{-1} = \sigma^2(F) + 0.0019F^2$). The maximum residual electron density in the final ΔF map was 0.62 eÅ^{-3} and the mean and maximum shifts/error in the final refinement cycle were 0.001 and 0.004 respectively. Computations were carried out on

an IBM PS/2 386 using the SHELXTL PC program system.[30] Atomic co-ordinates for non-hydrogen atoms are given in Table 2. Bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Tetracarbonyl(phenylsulfinylethene)iron(0) **18**.—Phenylsulfinylethene (0.75 g, 4.9 mmol) and $[Fe_2(CO)_9]$ (1.8 g, 4.9 mmol) were heated together under reflux in diethyl ether (100 cm^3) for 3.25 h under nitrogen. The resulting mixture was filtered through a plug of alumina (Brockmann 1, neutral; diethyl ether) and the yellow solution produced was evaporated under reduced pressure to give a yellow oil. Analysis of this oil by ^1H NMR spectroscopy showed that it contained the tetracarbonyl complex **18** and the hexacarbonyl di-iron complex **17** in a 55:2 ratio. In addition, a relatively small multiplet at δ 7.1–7.4 indicated the presence of the material previously tentatively assigned as a mixture of clusters containing at least iron carbonyl and phenyl groups, and very small signals at δ 2.76 (1 H, dd, *J* 11 and 3) and 4.55 (1 H, dd, *J* 11 and 8) may be attributable to the minor diastereoisomer of **18**. $\mathbf{18}_{maj}:\mathbf{18}_{min}$ = 55:1 (the third anticipated signal for $\mathbf{18}_{min}$ may be obscured by signals due to $\mathbf{18}_{maj}$). Subsequent column chromatography [SiO_2, Kieselgel 60; light petroleum (b.p. 60–80 °C)–diethyl ether, 4:1] led to the isolation of pure $\mathbf{18}_{maj}$ as yellow crystals (0.29 g, 55%) which were identical in all respects with the material isolated in the experiment described above.

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