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Synthesis and Reactivity of Iron Carbonyl Complexes of α,β-Unsaturated Acyl Silanes*

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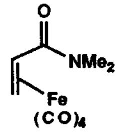
Abstract: 2-Trimethylsilyl-1-oxa-1,3-butadiene (**7**) reacts with $Fe_2(CO)_9$ to form an unstable tetracarbonyliron(0) complex (**8**) whereas 2-trimethylsilyl-4-phenyl-1-oxa-1,3-butadiene (**9**) and 2-(*tert*-butyldimethylsilyl)-4-phenyl-1-oxa-1,3-butadiene (**20**) react with $Fe_2(CO)_9$ to form highly stable crystalline tricarbonyliron(0) complexes (**16**) and (**21**). Complexes (**16**) and (**21**) both undergo acylation when reacted with methyl lithium under nitrogen to form γ-ketoacylsilanes [(**18**) and (**22**)], but only complex (**21**) reacts with methyl lithium under carbon monoxide to give the tricarbonyl(vinylketene)iron(0) complex (**23**).

The spectroscopic properties, synthesis and reactivity of acyl silanes have attracted the attention of organic chemists for over three decades and, although the relatively poor stability of acyl silanes towards light and basic conditions has perhaps retarded the anticipated rate of progress in this area, there is now a considerable volume of information available to facilitate new studies of this functional group.[1,2] As part of our current interest in the synthesis and reactivity of iron carbonyl complexes of α,β-unsaturated carbonyl compounds [exemplified by the specific structures (1)[3] and (2)[4,5]], we recently initiated a project designed to investigate whether or not complexes of the general type (3) and (4) could be synthesised.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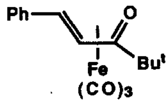
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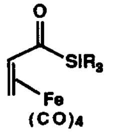
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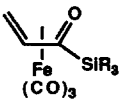
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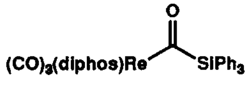
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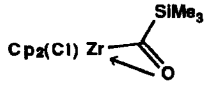
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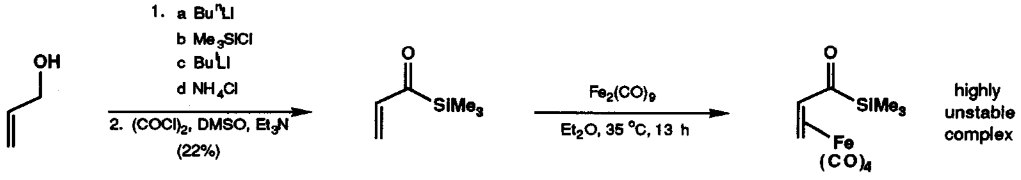
* Dedicated to Professor Charles W. Rees FRS on the occasion of his 65th birthday.

Our interest in these complexes was threefold. Firstly we wished to determine whether or not the C=O bond of acyl silanes can form stable Dewar-Chatt type bonds to transition metals as is implied in structure (4), because, to the best of our knowledge, this type of bonding has not yet been reported. [It is of note in this context that several transition metal-acyl silane complexes in which the acyl silane is bound to the transition metal *via* the bonding modes represented in structures (5)[6] and (6)[7] have been known for some time.] Secondly we were interested in evaluating whether or not complexes (3) and (4) could provide a relatively stable and storable source of α,β-unsaturated acyl silanes. And finally, we wished to determine whether or not complexes (3) and (4) would undergo reactions typical of the complexes represented by (1) and (2) thus extending the scope and flexibility of these systems.

RESULTS AND DISCUSSION

It was decided to begin the study with an examination of the reaction between di-iron nonacarbonyl [$Fe_2(CO)_9$] and the parent α,β-unsaturated acyl silane 2-trimethylsilyl-1-oxa-1,3-butadiene (7). The unsaturated acyl silane (7) was synthesised from allyl alcohol using a literature procedure.[8] *O*-Silylation of allyl alcohol followed by a retro-Brook rearrangement and a Swern oxidation gave the unstable acyl silane (7) in 22% yield from allyl alcohol. Due to the instability of compound (7) (w.r.t. polymer formation), it was immediately reacted with $Fe_2(CO)_9$ by stirring the two reagents together in diethyl ether at 35 °C for 13 h under a nitrogen atmosphere. Filtration through a short plug of alumina to remove iron residues and solvent evaporation gave a very unstable red oil which was examined by ^1H NMR spectroscopy. The spectrum contained essentially four broadened signals which were assigned as follows: δ 0.23 (9H, s, $SiMe_3$), 2.45 (1H, d, *J* 6, $CHH_{(E)}CHCOSiMe_3$), 2.79 (1H, d, *J* 12, $CHH_{(Z)}CHCOSiMe_3$) and 3.77 (1H, dd, *J* 12, 6, $CH_2CHCOSiMe_3$). On comparison of these values with those obtained from tetracarbonyliron(0) complexes of other α,β-unsaturated carbonyl complexes (*e.g.* tetracarbonyl(acrylamide)iron(0)[9] δ 2.70 (1H, dd, *J* 7.6, 1.9, $CHH_{(E)}CHCONH_2$), 2.94 (1H, dd, *J* 11.4, 1.9, $CHH_{(Z)}CHCONH_2$) and 3.64 (1H, dd, *J* 11.4, 7.6, $CH_2CHCONH_2$), the unstable red oil was tentatively assigned the structure (8) in which only the C=C bond of the α,β-unsaturated acyl silane is bound to the transition metal. Disappointingly, the extreme instability of the iron complex precluded its purification and examination by other spectroscopic techniques.



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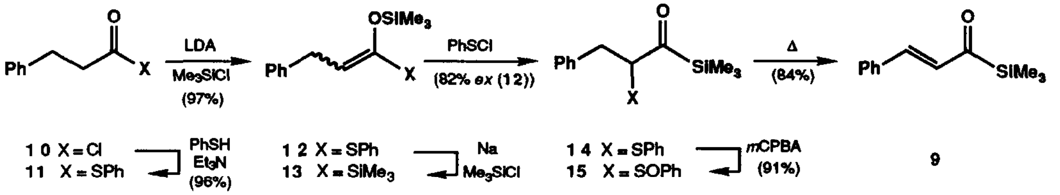
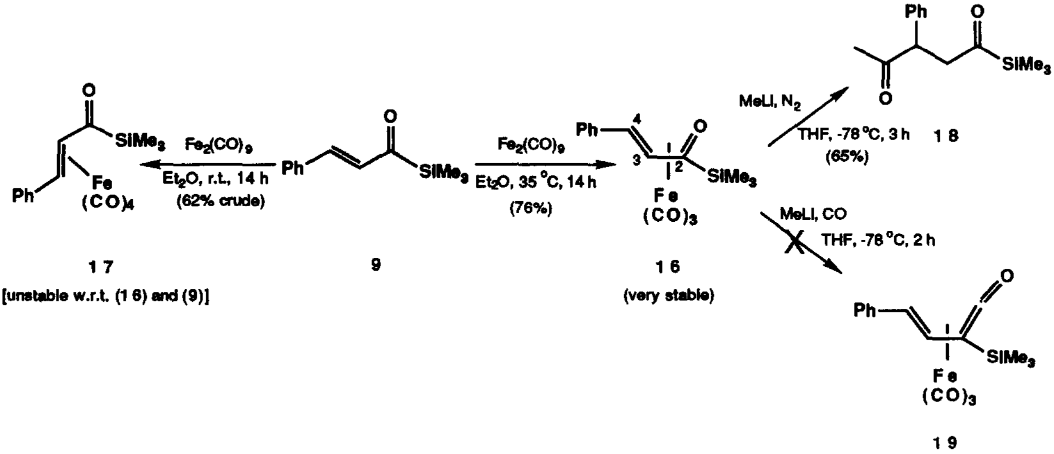
Disappointed by the instability of both acyl silane (7) and its iron complex (8), our attention turned to α,β-unsaturated acyl silanes bearing a β-phenyl substituent. Tricarbonyliron(0) complexes of β-phenyl-α,β-unsaturated ketones are considerably more stable than their β-unsubstituted or β-alkyl substituted analogues[10] and so it was anticipated that the iron complexes of 2-trimethylsilyl-4-phenyl-1-oxa-1,3-butadiene (9) should be more stable and easier to manipulate than complex (**8**). The β-phenyl substituted acyl silane (**9**) was synthesised by a route which has been outlined in the literature. 3-Phenylpropanoyl chloride (**10**) was converted into *S*-phenyl 3-phenylpropanethioate (**11**)[11] and this in turn was transformed into its trimethylsilyl enol ether (**12**).[12] Reductive silylation of (**12**), to give the acyl silane trimethylsilyl enol ether (**13**),[12] gave widely varying yields of (**13**) if the product was purified, and best results in this synthetic sequence were obtained when crude (**13**) was converted directly to the α-sulphenyl acyl silane (**14**).[13,14] Oxidation of (**14**) to the unstable α-sulphinyl substituted acyl silane (**15**)[13] and elimination of benzenesulphenic acid proceeded smoothly to give the desired α,β-unsaturated acyl silane (**9**)[13]. [Detailed experimental procedures for the complete synthesis of compound (**9**) and adequate characterisations of the intermediates generated *en route* were unavailable in the literature, and so experimental descriptions which should facilitate future syntheses of 2-trimethylsilyl-4-phenyl-1-oxa-1,3-butadiene (**9**) are provided below.]



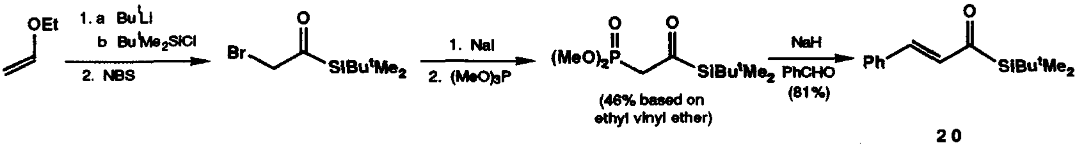
The relatively stable β-phenyl-α,β-unsaturated acyl silane (**9**) was initially stirred with $Fe_2(CO)_9$ in diethyl ether at 35 °C for 14 h. Filtration through a short plug of alumina and removal of solvent again produced a red oil but this time the product was much more stable and could easily be purified by chromatography. This produced red needles which were stable to heat, light and air and were identified on the basis of their microanalytical and spectroscopic data (IR, ^1H NMR, ^{13}C NMR and MS) as the tricarbonyliron complex (**16**). The IR spectrum of (**16**) contained three very strong $\nu_{C\equiv O}$ absorptions at 2067, 2009 and 1988 cm^{-1} but the absorptions ascribed to the C=C and C=O bonds in the IR spectrum of the ligand (**9**) at 1623 and 1581cm^{-1} respectively, were absent. Resonances at δ 3.41 (1H, d, *J* 9) and 6.03 (1H, d, *J* 9) in the ^1H NMR spectrum of (**16**) were assigned to the protons PhC*H*=CH and PhCH=C*H* respectively and these values were found to be consistent with values obtained for tricarbonyliron(0) complexes of β-phenyl-α,β-unsaturated ketones [*e.g.* δ 3.05 (d, *J* 10) and 6.1 (d, *J* 10) for complex (2)[4]]. The ^{13}C NMR spectrum of complex (**16**) contained resonances at δ 139.6/140.0, 88.1 and 67.9 assigned to C(2), C(3) and C(4) respectively and whilst these values are consistent with values obtained for complex (2)[4] [156.1, 71.6 and 60.8 for carbons (2)-(4)], they do suggest that the trimethylsilyl group may have a significant effect on the Dewar-Chatt bonding between the ligand and the transition metal. The mass spectrum of (**16**) contained a small M^+ ion and the microanalytical data obtained was in good agreement with the proposed structure.

In a separate experiment, the unsaturated acyl silane (**9**) was stirred with $Fe_2(CO)_9$ at room temperature in an attempt to isolate and identify the tetracarbonyliron(0) derivative (**17**). After filtration of the reaction mixture and solvent evaporation, a yellow oil remained which was predominantly material tentatively identified as the tetracarbonyliron(0) complex (**17**) on the basis of its IR and ^1H NMR spectra. The IR spectrum of the yellow oil contained four very strong $\nu_{C\equiv O}$ absorptions at 2095, 2033, 2021 and 1991 cm^{-1} and a weak absorption at 1598 cm^{-1} assigned to the uncomplexed C=O bond. Resonances at δ 4.72 (1H, d, *J* 11.5) and 5.07 (1H, d, *J* 11.5) in the ^1H NMR spectrum of the oil were attributed to the CH=CH protons. The yellow oil proved to be unstable with respect to the tricarbonyliron(0) complex (16) and all attempts to purify it, including chromatography at -50 °C, lead only to samples of (17) contaminated with (16) and ligand (9).

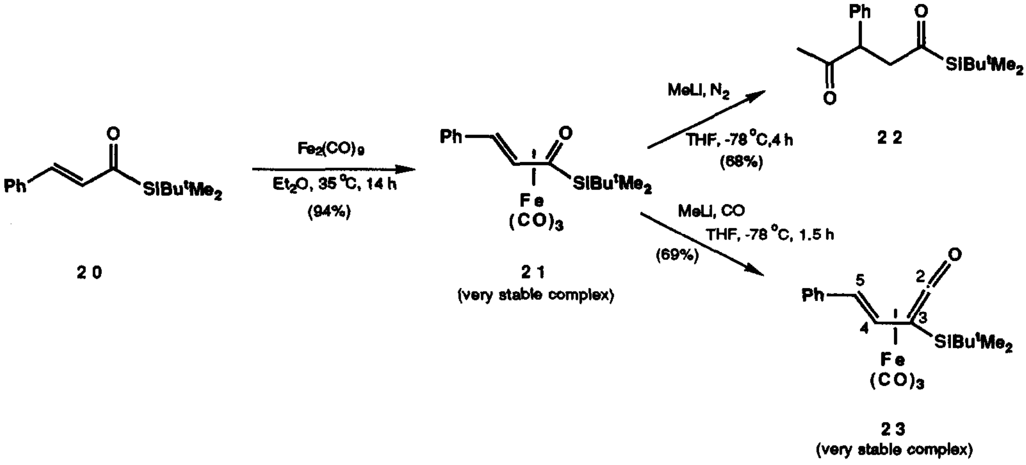
Having formed the tricarbonyliron(0) complex (16) in good yield (76%) and found it to be crystalline, stable and easy to handle, we wished to determine whether or not it would react in an analogous manner to tricarbonyliron(0) complexes of α,β-unsaturated ketones (*e.g.* 2). In particular we were interested in its reactivity towards alkyl lithium reagents under both a nitrogen and a carbon monoxide atmosphere. Under nitrogen, the α,β-unsaturated ketone complexes are known to react with alkyl lithium reagents to produce 1,4-diketones[4] whilst, in contrast, under carbon monoxide they react with alkyl lithium reagents to generate tricarbonyliron(0) complexes of vinylketenes.[5] Accordingly complex (16) was initially stirred with methyllithium under nitrogen at -78 °C for 3 h. After quenching and work-up, a pale yellow oil was obtained which on purification by chromatography produced a colourless oil. This was identified as the γ-keto acyl silane (18) on the basis of its spectroscopic data (IR, ^1H NMR, ^{13}C NMR and MS). Complex (16) was also reacted several times with methyl lithium under carbon monoxide at -78 °C. On each occasion, filtration of the product mixture through alumina and solvent removal gave a brown oil which ^1H NMR spectroscopy showed to contain an exceedingly complex mixture of products none of which was the desired vinylketene complex (19).



As the conversion of tricarbonyliron(0) complexes of vinylketones [(CO)$_3$(PhCH=CHCOR)Fe(0)] into tricarbonyliron(0) complexes of vinylketenes [(CO)$_3$(PhCH=CHC(C=O)R)Fe(0)] generally proceeds more efficiently as the steric demands of the alkyl substituent on the ketone are increased (R = Me, 35%; R = Bu^n, 48%; R = Pr^i, 82%; R = Bu^t, 93%),[5,15] we decided to investigate whether or not replacing the trimethylsilyl substituent in complex (16) with a bulkier silyl group would enable us to form the corresponding vinylketene complex. Accordingly the *tert*-butyldimethylsilyl substituted β-phenyl-α,β-unsaturated acyl silane (20) was synthesised from ethyl vinyl ether by a carefully documented and versatile literature procedure.[16,17]



The unsaturated acyl silane (20) was converted in excellent yield (94%) into its stable, crystalline and readily characterised tricarbonyliron(0) derivative (21) on stirring with $Fe_2(CO)_9$ at 35 °C. [Attempts to observe the corresponding tetracarbonyliron(0) complex by reacting (20) with $Fe_2(CO)_9$ at r.t. for 14 h, r.t. for 0.5 h and 0 °C for 2 h gave only mixtures of starting material (20) and its tricarbonyliron(0) complex (21).] Reaction of complex (21) with methyl lithium under nitrogen gave the γ-keto acyl silane (22) which was isolated and characterised. Gratifyingly addition of methyl lithium to complex (21) under a carbon monoxide atmosphere led to the isolation of highly stable yellow needle crystals which were identified on the basis of their microanalytical and spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, MS) as the silicon substituted vinylketene complex (23). The IR spectrum of (23) contained three very strong $\nu_{C=O}$ absorptions at 2058, 1999 and 1991 cm^{-1} and a medium absorption at 1795 cm^{-1}, a value typical of vinylketene ligands attached to tricarbonyliron(0) centres.[5] Resonances at δ 3.33 (1H, d, *J* 9.5) and 6.00 (1H, d, *J* 9.5) were assigned to the protons PhC*H*=CH and PhCH=C*H* respectively and these values were found to be consistent with values obtained for the CMe_3 analogue of complex (23) {i.e. [(CO)$_3$(PhCH=CHC(C=O)Bu^t)Fe(0)]} which were δ 3.14 (1H, d, *J* 9) and 6.34 (1H, d, *J* 9).[5] The ^{13}C NMR spectrum of complex (23) contained resonances at δ 230.3, 26.3, 93.7 and 67.4 assigned to C(2), C(3), C(4) and C(5) respectively and comparison with the corresponding values for the CMe_3 analogue (δ 232.4, 60.5, 91.8 and 59.4[5]) revealed a significant shielding effect on C(3). The mass spectrum of (23) contained a small M$^+$ ion and the microanalytical data obtained was in agreement with the proposed structure.



CONCLUSIONS

For the first time, acyl silanes have been shown to form stable Dewar-Chatt bonds to a transition metal fragment. From a practical and synthetic point of view, the easily synthesised α,β-unsaturated acyl silane 2-(*tert*-butyldimethylsilyl)-4-phenyl-1-oxa-1,3-butadiene (**20**) is readily converted into its tricarbonyliron(0) derivative (**21**) in high yield and this complex undergoes reactions typical of tricarbonyliron(0) complexes of α,β-unsaturated ketones. The reactions may be used to generate γ-keto acyl silanes,[18] a class of acyl silanes whose reactivity has essentially been unexplored to date, and vinylketene complexes whose reactivity has already been demonstrated to be diverse[5,19-21] and is currently unfolding still further.[15] Disappointingly, tetracarbonyliron(0) complexes of α,β-unsaturated acyl silanes, which, it was envisaged, might have acted as a crystalline and stable source of acyl silanes, have proved elusive to date.

EXPERIMENTAL

Reactions under nitrogen were performed using standard vacuum line and Schlenk tube techniques.[22] Tetrahydrofuran was distilled from sodium benzophenone ketyl. Diethyl ether was dried over Na wire. Dichloromethane was distilled from P_4O_{10}. Petroleum ether refers to the fraction boiling in the range 40-60 °C. $Fe_2(CO)_9$,[23] 2-trimethylsilyl-1-oxa-1,3-butadiene (**7**)[8] and 2-(*tert*-butyldimethylsilyl)-4-phenyl-1-oxa-1,3-butadiene (**20**)[15,16] were prepared using literature procedures. The concentration of MeLi and BuLi was determined by titration against diphenylacetic acid.[24] Triethylamine and diisopropylamine were refluxed over calcium hydride and distilled onto potassium hydroxide. Chlorotrimethylsilane was freshly distilled from sodium. 100% *m*CPBA was obtained by purifying commercially available 50-60% *m*CPBA.[25] PhSCl was prepared by adding sulphuryl chloride (3 equiv.) dropwise to a solution of PhSH in dichloromethane at -78 °C. After stirring for 0.5 h at -78 °C and 1 h at r.t., solvent removal gave PhSCl which was used as described below. All other reagents were used as obtained from commercial sources.

M.p.s were obtained using a Gallenkamp capillary m.p. apparatus and are uncorrected. The m.p.s of the iron complexes were measured in a sealed capillary under nitrogen. Elemental analyses were performed by Imperial College Microanalytical Service. IR spectra were obtained on a Perkin-Elmer 1710 FTIR instrument. NMR spectra were recorded on Jeol GSX 270 (270 MHz ^{1}H, 67.9 MHz ^{13}C) and Bruker AM 500 (500 MHz ^{1}H, 125.8 MHz ^{13}C) spectrometers; J values are given in Hz. Mass spectra were recorded 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 and CI techniques.

Tetracarbonyl(2-trimethylsilyl-1-oxa-1,3-butadiene)iron(0) (8).- 2-Trimethylsilyl-1-oxa-1,3-butadiene (7) (0.200 g, 1.56 mmol) and di-iron nonacarbonyl (1.10 g, 3.02 mmol) were stirred in diethyl ether (7 cm^3) at 35 °C for 13 h under a nitrogen atmosphere. The reaction mixture was then filtered through a short plug of alumina and eluted with diethyl ether. The solvent was removed *in vacuo* and the resulting unstable red oil was examined by ^{1}H NMR spectroscopy; δ_H ($CDCl_3$, 270 MHz) 0.23 (9H, s, $SiMe_3$), 2.45 (1H, d, J 6, $CH\mathit{H}_{(E)}CHCOSiMe_3$), 2.79 (1H, d, J 12, $CH\mathit{H}_{(Z)}CHCOSiMe_3$) and 3.77 (1H, dd, J 12, 6, $CH_2C\mathit{H}COSiMe_3$).

S-Phenyl 3-phenylpropanethioate (11).[11]- 3-Phenylpropanoyl chloride (**10**) (17.8 g, 0.106 mol), thiophenol (12.0 cm^3, 12.9 g, 0.117 mol) and triethylamine (15.0 cm^3, 10.9 g, 0.108 mol) were heated to reflux in toluene for 17 h. The resulting gelatinous mass was diluted with diethyl ether (60 cm^3) and then washed with 10% aqueous sodium hydroxide (2 x 30 cm^3), water (2 x 30 cm^3) and saturated brine (2 x 30 cm^3). The organic layer was dried ($MgSO_4$), filtered and reduced to dryness *in vacuo*. The resulting pale yellow crystalline mass was then recrystallised from ethyl acetate and hexane to give analytically pure *S*-phenyl 3-phenylpropanethioate (**11**) as white needles (24.35 g, 96%), m.p. 49-50 °C (Found: C, 74.05; H, 5.79. $C_{15}H_{14}OS$ requires C, 74.34; H, 5.82); ν_{max} (nujol)/cm^{-1} 1699s (C=O); δ_H ($CDCl_3$, 270 MHz) 3.0 (4H, m, CH_2CH_2), 7.15-7.4 (10H, m, 2 x Ph); δ_C ($CDCl_3$, 67.9 MHz), 31.4 (C(3)), 45.1 (C(2)), 126.4 (1 x C_{para}), 127.7 (1 x C_{ipso}), 128.4, 128.6, 129.2 (3 x C_{ortho} or C_{meta}), 129.4 (1 x C_{para}), 134.5 (1 x C_{ortho} or C_{meta}), 139.9 (1 x C_{ipso}) and 196.6 (C=O); *m/z* (EI) 242 (M$^+$, 4.5%), 133 (67, M-SPh), 105 (88, M-COSPh) and 91 (100, C_7H_7).

3-Phenyl-1-phenylsulphenyl-1-trimethylsiloxypropene (12).[12]- Butyl lithium (2.5 M, 4.4 cm^3, 0.011 mol) was added dropwise to diisopropylamine (1.5 ml, 1.08 g, 0.011 mol) in tetrahydrofuran (10 cm^3) at -78 °C under a nitrogen atmosphere. After stirring at room temperature for 0.5 h, the lithium diisopropylamide was added dropwise to a solution of *S*-phenyl 3-phenylpropanethioate (**11**) (2.42 g, 0.010 mol) in tetrahydrofuran (100 cm^3) at -78 °C over a period of 10 min. After stirring at -78 °C for 1 h, the pale yellow mixture was treated with chlorotrimethylsilane (1.4 ml, 1.20 g, 0.011 mol) and allowed to warm to room temperature. After stirring for 2 h at room temperature, the solvent was removed *in vacuo* to give a thick sludge which was dissolved in petroleum ether and filtered through a cotton wool pad and sinter. Solvent removal *in vacuo* gave a translucent oil which was identified as a 1:1 mixture of geometric isomers of 3-phenyl-1-phenylsulphenyl-1-trimethylsiloxypropene (**12**) (3.04 g, 97%) and was used in the next stage without further purification; ν_{max} (liquid)/cm^{-1} 1625w (C=C), 1252m and 845s ($SiMe_3$); δ_H ($CDCl_3$, 270 MHz) 0.08 and 0.14 (9H, s, $SiC(CH_3)_3$), 3.47 and 3.62 (2H, d, *J* 7.3 (7.6), $PhCH_2$), 5.40 and 5.45 (1H, t, *J* 7.6 (7.3), $PhCH_2CH$) and 7.1-7.45 (5H, m, Ph); *m/z* (EI) 314 (M$^+$, 2%), 205 (5, M-SPh) and 73 (100, $SiMe_3$).

1-Trimethylsilyl-3-phenyl-2-phenylsulphenylpropan-1-one (14).[12-14]- Sodium (50% dispersion in paraffin, 3.64 g, 0.080 mol) was washed with 100-120 °C petroleum ether (6 x 20 cm^3) and benzene (20 cm^3). After the addition of benzene (35 cm^3), the resulting mixture was stirred at 0 °C whilst chlorotrimethylsilane (10.1 cm^3, 8.64 g, 0.080 mol) was carefully added dropwise over *ca* 15 min. After this addition was complete, the reaction mixture was allowed to warm to room temperature and stirred rapidly whilst a solution of 3-phenyl-1-phenylsulphenyl-1-trimethylsiloxypropene (**12**) (3.14 g, 0.01 mol) in benzene (15 cm^3) was added dropwise. The resulting mixture was then heated at reflux for 2 h during which time the grey suspension turned bright purple. Subsequent filtration through kieselguhr and solvent removal *in vacuo* gave a yellow oil. This was dissolved in petroleum ether (15 cm^3), washed with a tetrahydrofuran-water mixture (1:1) saturated with sodium bicarbonate (2 x 10 cm^3) and dried ($MgSO_4$). Filtration and solvent removal *in vacuo* gave a very pale yellow oil which was identified as a 3:2 isomeric mixture of 3-phenyl-1-trimethylsiloxy-1-trimethylsilylpropene (**13**) (2.51 g) by comparison of its ^1H NMR spectrum with literature values[11] [δ_H ($CDCl_3$, 270 MHz) 0.2-0.4 (18H, 4 x s, $SiMe_3$ and $OSiMe_3$), 3.45 and 3.5 (2H, 2 x d, *J* 8 and 7, $PhCH_2CH$), 5.3 and 5.7 (1H, t, *J* 7 and 8, $PhCH_2CH$) and 7.2-7.6 (5H, m, Ph)]. A solution of the crude 3-phenyl-1-trimethylsiloxy-1-trimethylsilylpropene (**13**) (2.51 g, 9.03 mmol) in tetrachloromethane (20 cm^3) was cooled to - 22 °C and a solution of PhSCl in tetrachloromethane was added portionwise until the orange colour of the PhSCl persisted. The reaction was stirred at -22 °C for 5 min. before it was diluted with petroleum ether (30 cm^3), washed with 5% aqueous sodium hydrogen carbonate (2 x 20 cm^3), water (2 x 20 cm^3) and saturated brine (2 x 20 cm^3). The organic layer was then dried ($MgSO_4$), filtered and reduced *in vacuo* to a dark orange oil. Purification by column chromatography (Sorbsil C60; petroleum ether-diethyl ether, 19:1) yielded 1-trimethylsilyl-3-phenyl-2-phenylsulphenylpropan-1-one (14) as a viscous orange oil [2.52 g, 82% based on 3-phenyl-1-phenylsulphenyl-1-trimethylsiloxypropene (12)], b.p. 150 °C (Kugelrohr oven temperature) at 0.2 mm Hg; ν_{max} (liquid)/cm^{-1} 1635s (C=O), 1250s and 844vs ($SiMe_3$); δ_H ($CDCl_3$, 270 MHz) 0.17 (9H, s, $SiMe_3$), 2.89 (1H, dd, *J* 14.2, 6.6, 1H of $PhCH_2$), 3.23 (1H, dd, *J* 14.2, 8.3, 1H of $PhCH_2$), 4.15 (1H, dd, *J* 8.3, 6.6, PhSC*H*) and 7.1-7.25 (10H, m, 2 x Ph); δ_C ($CDCl_3$, 67.9 MHz) -2.3 ($Si(CH_3)_3$), 34.8 ($PhCH_2$), 61.1 (PhSCH), 126.5 (1 x C_{para}), 127.9 (1 x C_{para}), 128.5, 129.0, 129.7 (3 x C_{ortho} or C_{meta}), 130.1 (1 x C_{ipso}), 132.7 (1 x C_{ortho} or C_{meta}), 138.7 (1 x C_{ipso}) and 236.4 ($COSiMe_3$); *m/z* (CI, NH_3) 205 (M^+-PhSH+1, 30%), 90 (100, $SiMe_3$ + NH_3).

1-Trimethylsilyl-3-phenyl-2-phenylsulphinylpropan-1-one (15).[13]- A solution of *m*CPBA (100%, 0.173 g, 1.00 mmol) in dichloromethane (10 cm^3) was added dropwise over *ca* 15 min. to a solution of 1-trimethylsilyl-3-phenyl-2-phenylsulphenylpropan-1-one (14) (0.314 g, 1.00 mmol) in dichloromethane (15 cm^3) at 0 °C. The reaction mixture was stirred for a further 15 min. at 0 °C and then allowed to warm to room temperature and stirred for a further 1 h. The product mixture was diluted with diethyl ether (40 cm^3) and the organic layer was washed with 10% aqueous sodium hydroxide (2 x 10 cm^3), water (2 x 10 cm^3) and saturated brine (2 x 20 cm^3). After drying over $MgSO_4$ and filtration, removal of the solvent from the organic layer gave a pale yellow viscous oil which was purified by column chromatography (Sorbsil C60, petroleum ether-diethyl ether, 7:3) to give 1-trimethylsilyl-3-phenyl-2-phenylsulphinylpropan-1-one (15) as an unstable pale yellow syrup and a 1:1 mixture of diastereoisomers (0.301 g, 91%); ν_{max} (liquid)/cm^{-1} 1630m (C=O), 1050m (S=O), 1250m and 842s ($SiMe_3$); δ_H ($CDCl_3$, 270 MHz) -0.48 (9H, s, $SiMe_3$), -0.04 (9H, s, $SiMe_3$), 2.73 (1H, dd, *J* 13.19, 3.67, 1H of $PhCH_2$), 2.97 (1H, dd, *J* 13.19, 11.23, 1H of $PhCH_2$), 3.43 (1H, dd, *J* 13.19, 11.28, 1H of $PhCH_2$), 3.46 (1H, dd, *J* 13.19, 3.91, 1H of $PhCH_2$), 4.62 (1H, dd, *J* 11.23, 3.67, $PhCH_2CH$), 4.62 (1H, dd, *J* 11.28, 3.91, $PhCH_2CH$) and 6.9-7.7 (5H, m, Ph); *m/z* (CI, NH_3) 205 (M^+-PhSOH+1, 100%).

2-Trimethylsilyl-4-phenyl-1-oxa-1,3-butadiene (9).[16]- 1-Trimethylsilyl-3-phenyl-2-phenylsulphinylpropan-1-one (15) (0.270 g, 0.818 mmol) was heated to reflux in hexane (30 cm^3) under nitrogen for 6 h. The resulting mixture was then washed successively with 5% aqueous sodium hydrogen carbonate (2 x 5 cm^3), water (2 x 5 cm^3) and saturated brine (2 x 10 cm^3). The hexane solution was then dried ($MgSO_4$), filtered and concentrated *in vacuo* to give crude (9). Purification by column chromatography (Merck Kieselgel 60; petroleum ether-diethyl ether, 19:1) gave previously uncharacterised 2-trimethylsilyl-4-phenyl-1-oxa-1,3-butadiene (9) as a brilliant orange oil (0.141 g, 84%), b.p. 100-102 °C at 0.5 mm Hg (Found: *m/z* 204.0970. $C_{12}H_{16}OSi$ requires 204.0970); ν_{max} (liquid)/cm^{-1} 1641m, 1623m (C=C), 1581s (1563sh) (C=O), 1250 and 844 ($SiMe_3$); δ_H (C_6D_6, 270 MHz) 0.14 (9H, s, $SiMe_3$), 6.87 (1H, d, *J* 16.4, PhCH=C*H*), 6.9-7.2 (5H, m, Ph) and 7.38 (1H, d, *J* 16.4, PhC*H*=CH); δ_C {^1H} ($CDCl_3$, 125.8 MHz) -2.0 ($Si(CH_3)_3$), 128.2 (C_{ortho} or C_{meta}), 128.9 (C_{ortho} or C_{meta}), 130.4 (C_{para} or C(3)), 131.3 (C_{para} or C(3)), 134.9 (C_{ipso}), 142.9 (C(4)) and 224.4 ($COSiMe_3$); *m/z* (CI, NH_3) 205 (M^++1, 100%).

Tricarbonyl(2-trimethylsilyl-4-phenyl-1-oxa-1,3-butadiene)iron(0) (16).- 2-Trimethylsilyl-4-phenyl-1-oxa-1,3-butadiene (9) (0.120 g, 0.59 mmol) and di-iron nonacarbonyl (0.481 g, 1.32 mmol) were stirred in diethyl ether (7 cm^3) at 35 °C for 14 h under a nitrogen atmosphere. The reaction mixture was then filtered through a short plug of alumina and eluted with diethyl ether. The solvent was removed *in vacuo* and the resulting red oil was purified by column chromatography (Merck Kieselgel 60; petroleum ether-diethyl ether, 19:1) and recrystallisation from pentane to give analytically pure *tricarbonyl(2-trimethylsilyl-4-phenyl-1-oxa-1,3-butadiene)iron(0)* (16) as red needles (0.156 g, 76%), m.p. 98-102 °C (decomp.) (Found: C, 52.38; H, 4.73. $C_{15}H_{16}FeO_4Si$ requires C, 52.34; H, 4.69%); ν_{max} (hexane)/cm^{-1} 2067vs, 2009vs, 1988vs (C≡O), 1298m and 846s (SiMe$_3$); δ_H (CDCl$_3$) 0.45 (9H, s, SiMe$_3$), 3.41 (1H, d, *J* 9, PhC*H*=CH), 6.03 (1H, d, *J* 9, PhCH=C*H*) and 7.2-7.35 (5H, m, Ph); δ_C {^{1}H} (CDCl$_3$, 125.8 MHz) 0.00 (SiMe$_3$), 67.9 (C(4)), 88.1 (C(3)), 128.5 (C$_{ortho}$ or C$_{meta}$), 129.0 (C$_{para}$), 130.6 (C$_{ortho}$ or C$_{meta}$)), 139.6 (C(2) or C$_{ipso}$), 140.0 (C(2) or C$_{ipso}$) and 211 (br, C≡O); *m/z* (EI) 344 (M$^+$, 0.7%), 316 (3.6, M-CO), 288 (5.0, M-2CO), 260 (19.4, M-3CO), 203 (25.6, M-Fe(CO)$_3$-H), 73 (100, SiMe$_3$).

Tetracarbonyl(2-trimethylsilyl-4-phenyl-1-oxa-1,3-butadiene)iron(0) (17).- 2-Trimethylsilyl-4-phenyl-1-oxa-1,3-butadiene (9) (0.081 g, 0.40 mmol) and di-iron nonacarbonyl (0.161 g, 0.44 mmol) were stirred in diethyl ether (7 cm^3) at room temperature for 14 h under a nitrogen atmosphere. The reaction mixture was then filtered through a short plug of alumina and eluted with diethyl ether. The solvent was removed *in vacuo* and the resulting yellow oil was subjected to low temperature column chromatography (-50 °C; Merck Kieselgel 60; petroleum ether-diethyl ether, 19:1). This gave *tetracarbonyl(2-trimethylsilyl-4-phenyl-1-oxa-1,3-butadiene)iron(0)* (17) as unstable yellow crystals (0.091 g, 62%) which became a yellow oil on storage at -18 °C overnight under nitrogen; ν_{max} (hexane)/cm^{-1} 2095s, 2033vs, 2021s, 1991vs (C≡O), 1598w (C=O), 1251w and 844m (SiMe$_3$); δ_H (CDCl$_3$, 270 MHz) 0.37 (9H, s, SiMe$_3$), 4.72 (1H, d, *J* 11.5, PhC*H*CH), 5.07 (1H, d, *J* 11.5, PhCHC*H*) and 7.2-7.6 (5H, m, Ph).

1-(Trimethylsilyl)-3-phenylpentan-1,4-dione (18).- Tricarbonyl(2-trimethylsilyl-4-phenyl-1-oxa-1,3-butadiene)-iron(0) (16) (0.106 g, 0.308 mmol) was dissolved in tetrahydrofuran (7 cm^3) and cooled to -78 °C under a nitrogen atmosphere. Methyl-lithium (1.44 M, 0.23 cm^3, 0.331 mmol) was added dropwise to the orange yellow solution whereupon it became deep orange. The resulting solution was stirred for 3 h at -78 °C and was then quenched with *tert*-butyl bromide (0.1 ml, 0.87 mmol). The resulting orange-brown solution was stirred for a further 0.5 h at -78 °C and then allowed to warm to room temperature. The black mixture obtained was then stirred at room temperature for a further 3 h. The THF was removed *in vacuo* and the resulting thick brown oil was added to chloroform (7 cm^3) and the suspension stirred under air for 6 h. Filtration of the mixture through a short plug of alumina and elution with diethyl ether gave a yellow solution which on concentration gave a pale yellow oil. Purification (Sorbsil C60; petroleum ether-diethyl ether, 97:3) gave *1-(trimethylsilyl)-3-phenylpentan-1,4-dione (18)* as a colourless oil (0.048 g, 65%), (decomp. 55 °C at 0.5 mm Hg) (Found: *m/z* 249.1310. $C_{14}H_{21}O_2Si$ requires 249.1311); ν_{max} (liquid)/cm^{-1} 1714s (MeC=O), 1639vs (Me$_3$SiC=O), 1252m and 846vs (SiMe$_3$); δ_H (CDCl$_3$, 270 MHz) 0.20 (9H, s, SiC(CH$_3$)$_3$), 2.13 (3H, s, CH$_3$CO), 2.70 (1H, dd, *J* 18.3, 3.4, 1H of C*H*$_2$COSiMe$_3$), 3.65 (1H, dd, *J* 18.3, 10.3, 1H of C*H*$_2$COSiMe$_3$), 4.23 (1H, dd, *J* 10.3, 3.4, PhC*H*COMe) and 7.2-7.35 (5H, m, Ph); δ_C {^{1}H} (CDCl$_3$, 67.9 MHz) -3.2 (SiMe$_3$), 29.1 (C5), 51.5 (C(2) or

C(3)), 52.8 (C(2) or C(3)), 127.4 (C_{para}), 128.2 (C_{ortho} or C_{meta}) 129.1 (C_{ortho} or C_{meta}), 138.3 (C_{ipso}), 207.1 (C(4)), 245.7 (C(1)); *m/z* (CI, NH_3) 249 (M^++1, 89%) and 73 (100, $SiMe_3$).

*Tricarbonyl[2-(*tert-*butyldimethylsilyl)-4-phenyl-1-oxa-1,3-butadiene]iron(0) (21)*.- 2-(*Tert*-butyldimethylsilyl)-4-phenyl-1-oxa-1,3-butadiene (**20**) (0.123 g, 0.50 mmol) and di-iron nonacarbonyl (0.404 g, 1.11 mmol) were stirred in diethyl ether (7 cm^3) at 35 °C for 14 h under a nitrogen atmosphere. The reaction mixture was filtered through a short plug of alumina and eluted with diethyl ether. The solvent was removed *in vacuo* and the resulting red solid was purified by column chromatography (Merck Kieselgel 60; petroleum ether-diethyl ether, 97:3) and recrystallisation from hexane to give analytically pure *tricarbonyl[2-(*tert-*butyldimethylsilyl)-4-phenyl-1-oxa-1,3-butadiene]iron(0)* (**21**) as red-orange crystals (0.182 g, 94%), m.p. 82-86 °C (decomp.) (Found: C, 56.16; H, 5.70. $C_{18}H_{22}FeO_4Si$ requires C, 55.96; H, 5.74%); ν_{max} (hexane)/cm^{-1} 2067vs, 2009vs, 1989vs (C≡O), 1260w and 837w ($SiBu^tMe_2$); δ_H ($CDCl_3$, 270 MHz) 0.23 (3H, s, SiMe), 0.57 (3H, s, SiMe), 1.04 (9H, s, $SiBu^t$), 3.44 (1H, d, *J* 9.5, PhC*H*=CH), 5.97 (1H, d, *J* 9.5, PhCH=C*H*) and 7.2-7.4 (5H, m, Ph); δ_C {^1H} ($CDCl_3$, 125.8 MHz) -7.5 (SiMe), -5.7 (SiMe), 16.9 (Si*C*Me$_3$), 26.4 (SiC(*C*H$_3$)$_3$), 66.1 (C(4)), 89.9 (C(3)), 126.8 (C_{ortho} or C_{meta}), 127.3 (C_{para}), 128.9 (C_{ortho} or C_{meta}), 136.8 (C(2) or C_{ipso}), 137.9 (C(2) or C_{ipso}) and 208 (br, C=O); *m/z* (EI) 386 (M^+, 0.5%), 358 (3.8, M-CO), 330 (9.3 M-2CO), 302 (26.2, M-3CO), 246 (6.5, M-Fe(CO)$_3$), 115 (22.5, $SiMe_2Bu^t$) and 73 (100, $SiMe_3$).

*1-(*Tert-*butyldimethylsilyl)-3-phenylpentan-1,4-dione (22)*.- Tricarbonyl(2-(*tert*-butyldimethylsilyl)-4-phenyl-1-oxa-1,3-butadiene)iron(0) (**21**) (0.100 g, 0.259 mmol) was dissolved in tetrahydrofuran (6 cm^3) and cooled to -78 °C under a nitrogen atmosphere. Methyl-lithium (1.42 M, 0.20 cm^3, 0.284 mmol) was added dropwise to the orange-yellow solution whereupon it became deep orange. The resulting solution was stirred for 4 h at -78 °C and was then quenched with *tert*-butyl bromide (0.1 ml, 0.87 mmol). The orange-brown solution was then allowed to warm to room temperature and the black mixture obtained was stirred at room temperature for a further 4 h. The THF was then removed *in vacuo* and the thick brown oil generated was added to chloroform (7 cm^3) and the light-brown suspension stirred under air for 6 h. Filtration of the mixture through a short plug of alumina and elution with diethyl ether gave a yellow solution which on concentration gave a pale yellow oil. Purification (Sorbsil C60; petroleum ether-diethyl ether, 97:3) gave *1-(*tert-*butyldimethylsilyl)-3-phenylpentan-1,4-dione (22)* as a colourless oil (0.051 g, 68%), (decomp. 68 °C at 0.5 mm Hg) (Found: *m/z* 291.1780. $C_{17}H_{27}O_2Si$ requires 291.1780); ν_{max} (liquid)cm^{-1} 1718s (MeC=O), 1640s (Me_3SiC=O), 1251m, 838m, 824m and 804m (Si-C); δ_H ($CDCl_3$, 270 MHz) 0.183 (3H, s, SiMe), 0.185 (3H, s, SiMe), 0.93 (9H, s, $SiBu^t$), 2.14 (3H, s, CH_3CO), 2.70 (1H, dd, *J* 18.6, 3.4, 1H of C*H*$_2$COSiMe$_2$Bu^t), 3.64 (1H, dd, *J* 18.6, 10.3, 1H of C*H*$_2$COSiMe$_2$Bu^t), 4.25 (1H, dd, *J* 10.3, 3.4, PhC*H*COMe) and 7.2-7.35 (5H, m, Ph); δ_C {^1H} ($CDCl_3$, 67.9 MHz) -7.07 (1 CH_3 of Si(CH$_3$)$_2$Bu^t), -7.03 (1 CH_3 of Si(CH$_3$)$_2$Bu^t), 16.6 (*C*(CH$_3$)$_3$), 26.4 (C(*C*H$_3$)$_3$), 29.1 (C5), 52.7 (C(2) or C(3)), 53.8 (C(2) or C(3)), 127.4 (C_{para}), 128.3 (C_{ortho} or C_{meta}) 129.1 (C_{ortho} or C_{meta}), 138.3 (C_{ipso}), 207.0 (C(4)), 244.9 (C(1)); *m/z* (CI, NH_3) 291 (M^++1, 100%).

*Tricarbonyl[3-(*tert-*butyldimethylsilyl)-5-phenyl-1-oxapenta-1,2,4-triene]iron(0) (23)*.- Methyl lithium (0.16 ml, 1.4 M, 0.228 mmol) was added dropwise to a stirred solution of tricarbonyl[2-(*tert*-butyldimethylsilyl)-4-phenyl-1-oxa-1,3-butadiene)]iron(0) (**21**) (0.080 g, 0.207 mmol) in tetrahydrofuran (7 cm^3) at -78 °C under a carbon monoxide atmosphere. After stirring at -78 °C for 1.5 h, the reaction mixture was allowed to warm to room temperature and stirred for a further 1 h. Filtration of the reaction mixture through a short plug of alumina and removal of solvent gave yellow crystals which were purified by column chromatography (Merck Kieselgel 60; 40-60 petroleum ether-ethyl acetate, 98:2). Recrystallisation of the resulting yellow crystals from hexane gave analytically pure yellow needles of *tricarbonyl[3-(*tert*-butyldimethylsilyl)-5-phenyl-1-oxapenta-1,2,4-triene]iron(0) (23)* (0.055 g, 69%) m.p. 116-118 °C (decomp.) (Found: C, 57.18; H, 5.30. $C_{19}H_{22}FeO_4Si$ requires C, 57.29; H, 5.57%); ν_{max} (hexane)/cm^{-1} 2058vs, 1999vs, 1991vs (C≡O) and 1 795m (C=O); δ_H ($CDCl_3$, 270 MHz) 0.088 (3H, s, SiMe), 0.095 (3H, s, SiMe), 0.95 (9H, s, SiC(C*H*$_3$)$_3$), 3.33 (1H, d, *J* 9.5, PhC*H*=CH), 6.00 (1H, d, *J* 9.5, PhCH=C*H*) and 7.25-7.35 (5H, m, Ph); δ_C $\{^1H\}$ ($CDCl_3$, 125.8 MHz) -8.0 (SiMe), -6.6 (SiMe), 18.0 (Si*C*Me$_3$), 26.3 (C(3)), 26.4 (SiC(*C*H$_3$)$_3$), 67.4 (C(5)), 93.7 (C(4)), 126.4 (C_{ortho} or C_{meta}), 127.8 (C_{para}), 129.1 (C_{ortho} or C_{meta}), 137.8 (C_{ipso}), 209 (br, C≡O), 230.3 (C(2)); *m/z* (EI) 398 (M^+, 0.4%) 370 (5.8, M-CO), 342 (13.5, M-2CO), 314 (2.6, M-3CO), 286 (28.9, M-4CO), 258 (62.1, M-$Fe(CO)_3$) and 73 (100, $SiMe_3$).

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