

Synthesis and reactivity of iron carbonyl complexes of β -silyl substituted α,β -unsaturated ketones

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β -Silyl α,β -unsaturated ketones, $R_3SiCH=CHC(O)Me$ ($R_3Si = Me_3Si, Bu^tMe_2Si, PhMe_2Si$), react with $[Fe_2(CO)_9]$ at 35 °C in diethyl ether to give tetracarbonyl $[R_3SiCH=CHC(O)Me]iron(0)$ complexes and at 55 °C in toluene to give tricarbonyl $[R_3SiCH=CHC(O)Me]iron(0)$ complexes. Tricarbonyl $[Me_3SiCH=CHC(O)Me]iron(0)$ and tricarbonyl $[Bu^tMe_2SiCH=CHC(O)Me]iron(0)$ react with methyllithium under a nitrogen atmosphere to give hexane-2,5-dione and 3-(*tert*-butyldimethylsilyl)hexane-2,5-dione, respectively, and with methyllithium under a carbon monoxide atmosphere to give the vinylketene complexes tricarbonyl(3-methyl-5-trimethylsilyl-1-oxa-1,2,4-triene)iron(0) and tricarbonyl(5-*tert*-butyldimethylsilyl-3-methyl-1-oxapenta-1,2,4-triene)iron(0) respectively.

We are currently interested in the synthesis and reactivity of tricarbonyliron(0) complexes of α,β -unsaturated ketones, a class of organometallic complex which until recently remained neglected in favour of tricarbonyliron(0) complexes of 1,3-dienes. We have demonstrated that tricarbonyliron(0) complexes of α,β -unsaturated ketones react with alkyllithium reagents under a nitrogen atmosphere to produce 1,4-diketones in good yield,¹ and that replacing the nitrogen atmosphere with a carbon monoxide atmosphere leads to the generation of tricarbonyliron(0) complexes of vinylketenes.² These stable crystalline derivatives of normally labile vinylketenes possess a rich and diverse chemistry: for example, they react with isonitriles³ and the anions of diethyl *N*-alkyl(aryl)phosphoramidates⁴ to give tricarbonyliron(0) complexes of vinylketenimines, with phosphonoacetate anions to give tricarbonyliron(0) complexes of vinylallenes,⁵ with nucleophiles to give β,γ -unsaturated organic carbonyl derivatives,⁶ with alkynes to give 1:1 adducts which may be converted into phenols and cyclopentenediones,⁷ and with alkenes to give decarbonylated 1:1 adducts which are precursors to cyclopropanes.⁸

Almost all of our exploratory work on the reactivity of tricarbonyliron(0) complexes of vinylketenes and vinylketenes has been based on α,β -unsaturated ketone complexes bearing a β -phenyl substituent. This is a reflection of the much greater stability of complexes of ligands bearing β -aryl substituents compared to those bearing β -alkyl substituents. Some of 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. In order to increase the scope and versatility of the reactions of tricarbonyl(vinylketone)iron(0) complexes, we have initiated a programme designed to find substituents other than aryl groups which will confer stability on these complexes. Ideally, these substituents should be synthetically useful functional groups and they should tolerate the reaction conditions used to convert the vinylketone complexes into 1,4-diketones and vinylketene complexes. Initially, sulfonyl and sulfanyl substituents were considered as candidates. Although both β -sulfonyl and β -sulfanyl α,β -unsaturated ketones gave heat and air stable tricarbonyliron(0) complexes which were easy to manipulate, neither of these classes of complex could be converted into 1,4-diketones, and only the sulfonyl substituted complexes could be converted into the corresponding vinylketene complexes (in low yield).⁹ A second set of candidates for the role of synthetically useful, stabilising and robust substituents are silyl groups. We

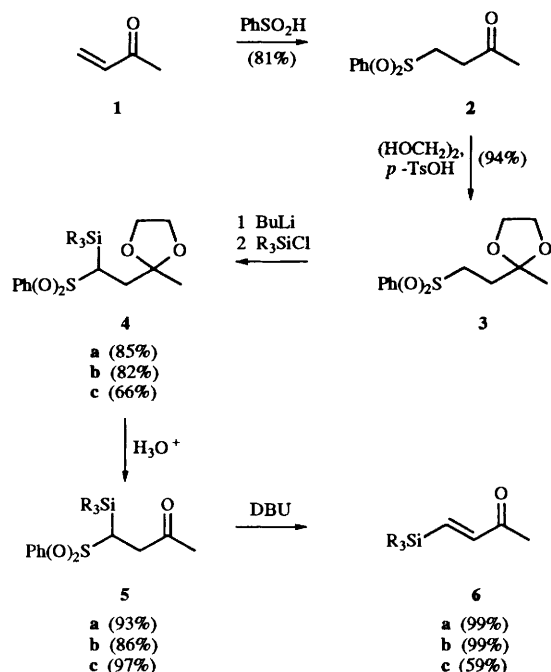
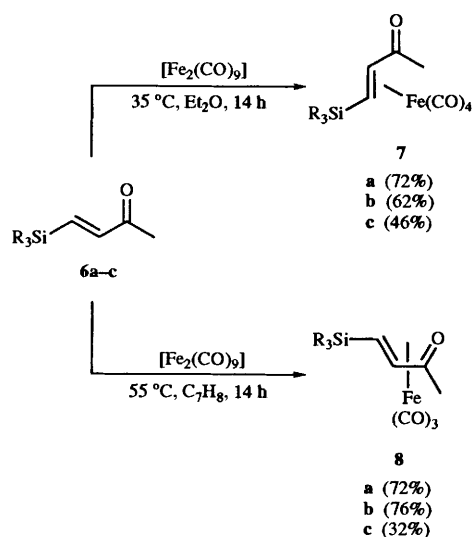
thus wished to determine whether or not these versatile functional groups¹⁰ would confer stability on tricarbonyliron(0) complexes of vinylketenes and, if so, whether or not the complexes so formed would react to give 1,4-diketone compounds and tricarbonyl(vinylketene)iron(0) complexes. The results of our study are presented below.

Results and discussion

The first compound selected for examination in our endeavour to determine whether or not β -silyl substituted α,β -unsaturated ketones form stable tricarbonyliron(0) complexes was 4-trimethylsilylbut-3-en-2-one **6a**. This was synthesised by a high-yielding literature procedure¹¹ in which the first step is the conjugate addition of benzenesulfonic acid to methyl vinyl ketone **1** to give 4-phenylsulfonylbutan-2-one **2**. The carbonyl of **2** was subsequently protected as its ethylene glycol acetal under azeotropic conditions to give 4-phenylsulfonylbutan-2-one ethylene acetal **3**. Compound **3** was then lithiated with BuLi and quenched with Me_3SiCl to give 4-phenylsulfonyl-4-trimethylsilylbutan-2-one ethylene acetal **4a**. Subsequent treatment with aqueous HCl generated 4-phenylsulfonyl-4-trimethylsilylbutan-2-one (**5a**) which was treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to generate the desired 4-trimethylsilylbut-3-en-2-one **6a** (Scheme 1).

In order to test whether or not compound **6a** would form stable iron carbonyl complexes, it was initially heated to reflux in diethyl ether under nitrogen with $[Fe_2(CO)_9]$ for 14 h. The resulting reaction mixture was filtered through alumina to remove the iron residues and the solvent removed *in vacuo* to give the crude reaction mixture as a dark orange oil. Investigation of the oil by ¹H NMR spectroscopy indicated that the major compound formed was a tetracarbonyliron(0) complex, not the desired tricarbonyliron(0) complex. This complex was isolated by chromatography and identified as novel tetracarbonyl(4-trimethylsilylbut-3-en-2-one)iron(0) **7a** on the basis of its IR, ¹H NMR, ¹³C NMR and mass spectra along with its microanalytical data. Of note are five absorptions in the IR spectrum at 2096, 2033, 2012, 1992 and 1682 cm⁻¹ assigned to the metal-bound carbonyls and the organic ketone respectively, and a peak at δ 203.5 in the ¹³C NMR spectrum which is attributed to the carbon of the organic ketone and indicates its unco-ordinated nature.

As relatively mild complexation conditions had generated the tetracarbonyliron(0) complex of **6a** rather than its desired

Scheme 1 a: $\text{R}_3\text{Si} = \text{Me}_3\text{Si}$; b: $\text{R}_3\text{Si} = \text{Bu}^t\text{Me}_2\text{Si}$; c: $\text{R}_3\text{Si} = \text{PhMe}_2\text{Si}$ a: $\text{R}_3\text{Si} = \text{Me}_3\text{Si}$; b: $\text{R}_3\text{Si} = \text{Bu}^t\text{Me}_2\text{Si}$; c: $\text{R}_3\text{Si} = \text{PhMe}_2\text{Si}$

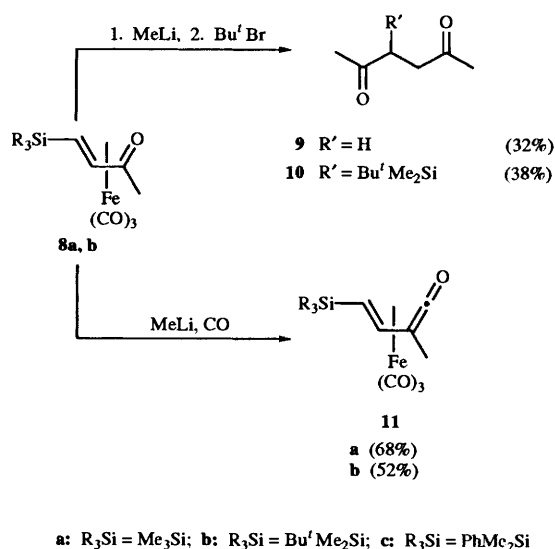
Scheme 2

tricyclopentadienyliron(0) derivative, somewhat harsher conditions were subsequently employed in order to try to effect the required decarbonylation. Thus, **6a** was heated with $[\text{Fe}_2(\text{CO})_9]$ under nitrogen in toluene at 55°C for 14 h. Filtration of the product mixture through a short plug of alumina, solvent removal and purification by column chromatography gave an orange oil that was identified as the desired novel tricyclopentadienyliron(0) complex **8a** on the basis of its spectroscopic data (Scheme 2). The IR spectrum of **8a** contained absorptions at 2069, 2009 and 1982 cm^{-1} assigned to the metal-bound carbonyls but no absorptions consistent with an unco-ordinated ketone, whilst a peak at $\delta 143.9$ in the ^{13}C NMR spectrum was assigned to the carbon of the metal co-ordinated ketone.

It is interesting at this point to contrast the successful

formation in good yields of the tetracarbonyliron(0) and tricarbonyliron(0) complexes of 4-trimethylsilylbut-3-en-2-one **6a** with attempts to form iron carbonyl complexes of its carbon analogue, 5,5-dimethylhex-3-en-2-one. Experiments in which this α,β -unsaturated ketone, formed by condensation of pivalaldehyde with acetone, was treated with $[\text{Fe}_2(\text{CO})_9]$ under several solvent and temperature conditions led only to very unstable dark orange oils. These gave only broadened NMR spectra and were too labile to be characterised further. It is tentatively postulated that the apparent stabilising effect of the silyl substituent is due to an interaction between a low-lying vacant silicon d orbital and a filled orbital associated with the metal complex.

With a stable tricarbonyliron(0) complex of a β -silyl substituted α,β -unsaturated ketone in hand, an investigation of its reactivity with respect to acylation and vinylketene formation was undertaken. A solution of complex **8a** in THF under an atmosphere of nitrogen was treated with methyllithium at -78°C for 30 min and then at room temperature for a further 30 min. After the reaction mixture had been cooled to -78°C and quenched with Bu^tBr , work-up and purification by column chromatography led to the isolation of a colourless oil which was identified as hexane-2,5-dione **9** by comparison of its spectroscopic data with those of literature values¹² (Scheme 3).



Scheme 3

On the other hand, when a solution of complex **8a** in THF under an atmosphere of carbon monoxide was treated with methyllithium at -78°C for 40 min and at room temperature for a further 1 h, subsequent work-up, column chromatography and crystallisation gave yellow needle crystals which were identified as the novel vinylketene complex tricarbonyl(3-methyl-5-trimethylsilyl-1-oxapenta-1,2,4-triene)iron(0) **11a**. Thus, although loss of the trimethylsilyl group had occurred during acylation of complex **8a** and the desired silylated product was not observed, it was gratifying at this point that conversion of complex **8a** into the desired silylated vinylketene complex **11a** had proceeded smoothly.

Encouraged by the formation of the vinylketene complex **11a** in good overall yield from the vinylketone **6a**, it was decided to investigate the effect of replacing the trimethylsilyl group with other silyl substituents. It was predicted that more bulky silyl groups would be less labile under the conditions required for acylation of their vinylketene complexes, and for conversion of their vinylketene complexes into the range of organometallic and organic derivatives formed from the phenyl substituted

analogues. Thus 4-*tert*-butyldimethylsilylbut-3-en-2-one **6b** and 4-dimethylphenylsilylbut-3-en-2-one **6c** were synthesised from the acetal **3** by the route used for the synthesis of **6a**. (The novel compounds **4-6b**, **4c** and **5c** were all fully characterised as was **6c** which had been synthesised previously by an entirely different route.¹³)

Reaction of **6b** and **6c** with $[\text{Fe}_2(\text{CO})_9]$ at either 35 °C in diethyl ether for 14 h or at 55 °C in toluene for 14 h gave the novel tetracarbonyliron(0) complexes **7b** and **7c**, and the novel tricarbonyliron(0) complexes **8b** and **8c**, respectively. Whilst the yields of the *tert*-butyldimethylsilyl derivatives **7b** and **8b** were very similar to those of the corresponding trimethylsilyl complexes **7a** and **8a**, the yields of the less stable dimethylphenylsilyl derivatives **7c** and **8c** were significantly lower. Thus, it was decided to progress only the *tert*-butyldimethylsilyl complex **8b** through to the reactivity stage of the investigation.

Reaction of the vinylketene complex **8b** with methyllithium under nitrogen gave, after work-up, a colourless oil which was identified, on the basis of its spectroscopic data, as the novel 1,4-diketone 3-(*tert*-butyldimethylsilyl)hexane-2,5-dione **10**. Thus, in contrast to the reaction of the trimethylsilyl derivative **8a**, the *tert*-butyldimethylsilyl substituent of **8b** survived the reaction and work-up conditions to give a relatively rare α -substituted ketone. In view of the synthetic potential of selectively silylated 1,4-diketones, it was disappointing that all attempts to increase the yield of this acylation reaction beyond 38% were unsuccessful. Finally, reaction of the vinylketene complex **8b** with methyllithium under carbon monoxide gave, after work-up, the novel complex tricarbonyl(5-*tert*-butyldimethylsilyl-3-methyl-1-oxapenta-1,2,4-triene)iron(0) **11b**.

To conclude, we have established that β -silyl α,β -unsaturated ketones form novel tricarbonyliron(0) complexes which may be characterised and used in further reactions. In particular, the trimethylsilyl and *tert*-butyldimethylsilyl vinylketene complexes **11a** and **11b** may be formed in good overall yield from the corresponding β -silyl α,β -unsaturated ketones. It is predicted that the products generated by treating these complexes with, for example, nucleophiles⁶ will ultimately prove to be more synthetically versatile than the corresponding styryl-containing products.

Experimental

Reactions under nitrogen and carbon monoxide were performed using standard vacuum line and Schlenk tube techniques.¹⁴ Tetrahydrofuran was distilled from sodium benzophenone ketyl. Diethyl ether was dried over Na wire. Dichloromethane was distilled from P_2O_{10} . Light petroleum refers to that boiling in the range 40–60 °C which was distilled before use. $[\text{Fe}_2(\text{CO})_9]$ was prepared using a literature procedure.¹⁵ The concentrations of MeLi and BuLi were determined by titration against diphenylacetic acid.¹⁶ All other reagents were used as obtained from commercial sources. All column chromatography was performed on Merck C-60. Mps were obtained on a Reichert 7905 hot-stage microscope and a Gallenkamp capillary mp apparatus and are uncorrected. The mps of organoiron 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 in CDCl_3 at room temperature on JEOL GSX 270 (270 MHz ^1H , 67.9 MHz ^{13}C) and Bruker AM 500 (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 EPSRC Mass Spectrometry Service Centre, Swansea, and on a VG Micromass 7070E instrument at Imperial College using EI, CI and FAB (*m*-nitrobenzyl alcohol matrix¹⁷) techniques.

4-Phenylsulfonylbutan-2-one **2**¹¹

To an acetic acid solution (100 cm^3) of sodium benzenesulfinate (15.0 g, 91.5 mmol) was added methyl vinyl ketone **1** (4.16 cm^3 , 3.50 g, 50.0 mmol). The reaction mixture was stirred at room temperature for 14 h and then diluted with water (100 cm^3) and half saturated aqueous NaHCO_3 (10 \times 100 cm^3). The resulting product mixture was then extracted with toluene (3 \times 50 cm^3) and the combined organic fractions were washed with water (2 \times 100 cm^3) and saturated brine (2 \times 100 cm^3), dried (MgSO_4), filtered and evaporated under reduced pressure to give the crude product. This was recrystallised from light petroleum (bp 80–100 °C) to give **2** as white needles (8.62 g, 40.7 mmol, 81%), mp 88–89 °C (Found: C, 56.5; H, 5.9. $\text{C}_{10}\text{H}_{12}\text{O}_3\text{S}$ requires C, 56.58; H, 5.70%); $\nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$ 1713s (C=O), 1304s and 1145s (SO_2); $\delta_{\text{H}}(270 \text{ MHz})$ 2.18 (3 H, s, Me), 2.93 (2 H, t, J 7.1, $\text{PhSO}_2\text{CH}_2=\text{CH}_2$), 3.37 (2 H, t, J 7.1, $\text{PhSO}_2\text{CH}_2=\text{CH}_2$), 7.65 (3 H, m, Ph) and 7.90 (2 H, m, Ph); $\delta_{\text{C}}(67.8 \text{ MHz})$ 29.8 (Me), 35.8 ($\text{PhSO}_2\text{CH}_2=\text{CH}_2$), 50.5 ($\text{PhSO}_2\text{CH}_2=\text{CH}_2$), 127.9 (C_{ortho} or C_{meta}), 129.4 (C_{ortho} or C_{meta}), 133.9 (C_{para}), 138.9 (C_{ipso}) and 203.7 (C=O); m/z (CI, NH_3) 230 $[(\text{MH} + \text{NH}_3)^+]$, 100%.

4-Phenylsulfonylbutan-2-one ethylene acetal **3**¹¹

Compound **2** (7.60 g, 35.8 mmol), ethylene glycol (10 cm^3) and toluene-*p*-sulfonic acid (0.10 g, 0.58 mmol) were dissolved in toluene (60 cm^3) and heated to reflux for 18 h to remove water azeotropically. The organic layer was washed with water (2 \times 50 cm^3) and saturated brine (2 \times 50 cm^3), dried (MgSO_4), filtered and evaporated under reduced pressure to give the crude product which was purified by chromatography [Al_2O_3 ; diethyl ether–light petroleum (3:7)] to give **3** as a white crystalline solid (8.61 g, 33.6 mmol, 94%) [Found: m/z 257.0850. $\text{C}_{12}\text{H}_{17}\text{O}_4\text{S}$ (MH) requires 257.0847]; $\nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$ 1586w (Ph), 1308s and 1148s (SO_2); $\delta_{\text{H}}(270 \text{ MHz})$ 1.26 (3 H, s, Me), 2.05 (2 H, m, $\text{PhSO}_2\text{CH}_2\text{CH}_2$), 3.16 (2 H, m, $\text{PhSO}_2\text{CH}_2\text{CH}_2$), 3.89 (4 H, m, $\text{OCH}_2\text{CH}_2\text{O}$), 7.57 (3 H, m, Ph) and 7.90 (2 H, m, Ph); $\delta_{\text{C}}\{^1\text{H}\}$ (67.8 MHz) 24.1 (Me), 31.9 ($\text{PhSO}_2\text{CH}_2\text{CH}_2$), 51.6 ($\text{PhSO}_2\text{CH}_2\text{CH}_2$), 64.8 ($\text{OCH}_2\text{CH}_2\text{O}$), 108.2 ($\text{PhSO}_2\text{CH}_2\text{CH}_2\text{CMe}$), 128.1 (C_{ortho} or C_{meta}), 129.3 (C_{ortho} or C_{meta}), 133.7 (C_{para}) and 139.1 (C_{ipso}); m/z (CI, NH_3) 257 (MH^+ , 100%) and 213 ($\text{MH} - \text{CH}_2\text{CH}_2\text{O}$, 40).

4-Phenylsulfonyl-4-trimethylsilylbutan-2-one ethylene acetal **4a**¹¹

A THF solution (50 cm^3) of compound **3** (2.56 g, 10.0 mmol) and 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (DMPU) (2.71 cm^3 , 2.87 g, 22.4 mmol) was cooled to –78 °C under an atmosphere of nitrogen. Butyllithium (2.1 mol dm^{-3} ; 7.1 cm^3 , 14.9 mmol) was added dropwise to the solution which was then stirred at –78 °C for a further hour. The reaction was then quenched by addition of chlorotrimethylsilane (3.0 cm^3 , 2.57 g, 23.6 mmol) to the mixture after which it was stirred for a further hour at –78 °C and then 1 h at room temperature. The resulting reaction mixture was poured into water (50 cm^3) and extracted with toluene (3 \times 50 cm^3). The combined organic fractions were washed with water (2 \times 50 cm^3) and saturated brine (2 \times 50 cm^3), dried (MgSO_4), filtered and evaporated under reduced pressure to give the crude product which was purified by chromatography (SiO_2 ; diethyl ether–light petroleum, 3:7) and then recrystallised from light petroleum (bp 80–100 °C) to give **4a** as white crystals (2.77 g, 8.45 mmol, 85%), mp 74–75 °C [Found: m/z 329.1242. $\text{C}_{15}\text{H}_{24}\text{O}_4\text{SSi}$ (MH) requires 329.1242]; $\nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$ 1299s and 1140s (SO_2), 1249s and 850s (C-Si); $\delta_{\text{H}}(270 \text{ MHz})$ 0.33 (9 H, s, SiMe_3), 0.98 (3 H, s, Me), 2.09 [1 H, dd, J 15.9, 4.6, $\text{PhSO}_2\text{CH}(\text{SiMe}_3)\text{CH}_2$], 2.24 [1 H, dd, J 15.9, 3.4, $\text{PhSO}_2\text{CH}(\text{SiMe}_3)\text{CH}_2$], 2.84 [1 H, dd, J 4.6, 3.4, $\text{PhSO}_2\text{CH}(\text{SiMe}_3)\text{CH}_2$], 3.67 (4 H, m, $\text{OCH}_2\text{CH}_2\text{O}$), 7.45 (3 H, m, Ph) and 7.72 (2 H, m, Ph); $\delta_{\text{C}}(67.8 \text{ MHz})$ 0.6 (SiMe_3),

23.7 (Me), 34.8 (PhSO₂CHCH₂), 51.4 (PhSO₂CHCH₂), 64.3 and 64.4 (OCH₂CH₂O), 108.3 (C-2), 128.2 (C_{ortho} or C_{meta}), 128.6 (C_{ortho} or C_{meta}), 132.7 (C_{para}) and 141.4 (C_{ipso}); *m/z* (CI, NH₃) 329 [(M + H)⁺, 62%] and 187 (MH – PhSO₂, 100).

4-Phenylsulfonyl-4-trimethylsilylbutan-2-one **5a**¹¹

Compound **4a** (1.20 g, 3.66 mmol) was dissolved in 5 mol dm⁻³ HCl (10 cm³) and acetone (10 cm³) and the mixture stirred at room temperature for 16 h. It was then diluted with water (50 cm³) and extracted with toluene (3 × 20 cm³). The combined extracts were washed with water (2 × 20 cm³) and saturated brine (2 × 20 cm³), dried (MgSO₄), filtered and evaporated under reduced pressure to give the crude product which was purified by chromatography [SiO₂; diethyl ether–light petroleum (3:7)] to give **5a** as a colourless oil (0.970 g, 3.41 mmol, 93%); *v*_{max}(Nujol)/cm⁻¹ 1721s (C=O), 1302s and 1116s (SO₂), 1254s and 853s (C-Si); δ_{H} (270 MHz) 0.25 (9 H, s, SiMe₃), 1.95 (3 H, s, Me), 2.62 [1 H, dd, *J* 19.3, 4.9, PhSO₂CH(SiMe₃)CH₂], 2.93 [1 H, dd, *J* 19.3, 6.1, PhSO₂CH(SiMe₃)CH₂], 3.63 [1 H, dd, *J* 6.1, 4.9, PhSO₂CH(SiMe₃)CH₂], 7.53 (3 H, m, Ph) and 7.84 (2 H, m, Ph); δ_{C} {¹H} (67.8 MHz) –1.4 (SiMe₃), 29.5 (Me), 39.6 [PhSO₂CH(SiMe₃)CH₂], 49.9 [PhSO₂CH(SiMe₃)CH₂], 127.9 (C_{ortho} or C_{meta}), 129.0 (C_{ortho} or C_{meta}), 133.2 (C_{para}), 140.5 (C_{ipso}) and 203.6 (C=O).

4-Trimethylsilylbut-3-en-2-one **6a**¹¹

Compound **5a** (0.284 g, 1.00 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.30 cm³, 0.305 g, 2.01 mmol) were heated to reflux in dichloromethane (5 cm³) under an atmosphere of nitrogen for 1 h. The resulting reaction mixture was then loaded onto SiO₂ and eluted [diethyl ether–light petroleum (1:9)] to give compound **6a** as a colourless oil (0.140 g, 0.986 mmol, 99%); *v*_{max}(neat)/cm⁻¹ 1681s (C=O), 1252s and 843s (C-Si); δ_{H} (270 MHz) 0.15 (9 H, s, SiMe₃), 2.28 (3 H, s, Me), 6.45 (1 H, d, *J* 19.3, Me₃SiCHCH) and 7.04 (1 H, d, *J* 19.3, Me₃SiCHCH); δ_{C} {¹H} (67.8 MHz) –2.1 (SiMe₃), 26.0 (Me), 142.9 (Me₃SiCHCH), 147.2 (Me₃SiCHCH) and 198.1 (C=O).

Tetracarbonyl(4-trimethylsilylbut-3-en-2-one)iron(0) **7a**

Compound **6a** (0.142 g, 1.00 mmol) and [Fe₂(CO)₉] (0.450 g, 1.24 mmol) were heated in diethyl ether (15 cm³) at 35 °C for 14 h under an atmosphere of nitrogen. The resulting mixture was filtered through an alumina plug to remove the iron residues after which it was evaporated under reduced pressure to give the crude product as a dark orange oil which was purified by chromatography [SiO₂; diethyl ether–light petroleum (5:95)] to give the *title compound* **7a** as an orange oil which was crystallised from chloroform–light petroleum to give rhombic crystals (0.220 g, 0.720 mmol, 72%); mp 54–55 °C (Found: C, 42.8; H, 4.3%. C₁₁H₁₄FeO₅Si requires C, 42.60; H, 4.55%); *v*_{max}(hexane)/cm⁻¹ 2096vs, 2033vs, 2012vs and 1992vs (C=O), 1682w (C=O), 1252w and 842w (C-Si); δ_{H} (270 MHz) 0.13 (9 H, s, SiMe₃), 2.34 (3 H, s, Me), 2.79 (1 H, d, *J* 13.2, C-3) and 3.50 (1 H, d, *J* 13.2, C-4); δ_{C} {¹H} (67.8 MHz) 0.4 (SiMe₃), 29.1 (Me), 42.8 (C-3), 59.5 (C-4), 203.3 (C=O) and 208.1 (C=O); *m/z* (FAB) 310 (M⁺, 21%) and 73 (Me₃Si, 100).

Tricarbonyl(4-trimethylsilylbut-3-en-2-one)iron(0) **8a**

Compound **6a** (0.144 g, 1.01 mmol) and [Fe₂(CO)₉] (0.800 g, 2.20 mmol) were heated in toluene at 55 °C for 14 h under an atmosphere of nitrogen. The resulting mixture was filtered through an alumina plug to remove the iron residues after which it was evaporated under reduced pressure to give the crude product as a dark orange oil which was purified by chromatography [SiO₂; diethyl ether–light petroleum (5:95)] to give the *title compound* **8a** as an orange oil (0.204 g, 0.723 mmol, 72%) (Found: *m/z* 283.0090. C₁₀H₁₅FeO₄Si requires 283.0089); *v*_{max}(hexane)/cm⁻¹ 2069vs, 2009vs and 1982 (C=O), 1252m and 837m (C-Si); δ_{H} (270 MHz) 0.12 (9 H, s, SiMe₃), 1.11

(1 H, d, *J* 10.7, Me₃SiCH=CH), 2.50 (3 H, s, Me) and 5.60 (1 H, d, *J* 10.7, Me₃SiCH=CH); δ_{C} {¹H} (67.8 MHz) –0.4 (SiMe₃), 20.9 (Me), 48.9 (Me₃SiCHCH), 85.1 (Me₃SiCHCH), 143.9 (C=O) and 208.2 (C=O); *m/z* (FAB) 283 (MH⁺, 100%), 255 (MH – CO, 36) and 226 (M – 2CO, 27).

Hexane-2,5-dione **9**¹²

A solution of compound **8a** (0.0860 g, 0.305 mmol) in THF (15 cm³) was cooled to –78 °C and methyllithium (1.5 mol dm⁻³; 0.23 cm³, 0.345 mmol) was added dropwise to it. The mixture was stirred first at –78 °C for 30 min and then at room temperature for 30 min after which the resulting dark red solution was cooled to –78 °C and quenched with Bu^tBr (0.10 cm³, 0.12 g, 0.88 mmol). After the reaction mixture had been allowed to warm to room temperature it was further stirred for 1 h and then evaporated under reduced pressure. The residue was dissolved in chloroform (10 cm³) and the solution stirred for 2 h before filtration through alumina to remove the iron residues and evaporation to give a crude product. Purification [SiO₂; diethyl ether–light petroleum (1:9)] led to the isolation of **9** as a colourless oil (11 mg, 0.096 mmol, 32%); *v*_{max}(neat)/cm⁻¹ 1713s (C=O); δ_{H} (270 MHz) 2.19 (6 H, s, Me) and 2.70 (4 H, s, CH₂); *m/z* (EI) 114 (M⁺, 4%), 99 (M – Me, 26) and 43 (MeCO, 100).

Tricarbonyl(3-methyl-5-trimethylsilyl-1-oxapenta-1,2,4-triene)iron(0) **11a**

Compound **8a** (0.140 g, 0.496 mmol) was dissolved in THF (15 cm³), and the solution cooled to –78 °C whilst being continuously purged with CO. Methyllithium (1.44 mol dm⁻³; 0.38 cm³, 0.55 mmol) was added dropwise to the reaction mixture which was then stirred at –78 °C for 40 min. After removal of the cooling bath the reaction mixture was allowed to warm to room temperature at which it was stirred for a further 1 h. The resulting dark brown mixture was filtered through alumina and then evaporated under reduced pressure to give an orange oil, chromatography [SiO₂; diethyl ether–light petroleum (1:19)] and crystallisation of which afforded the *title compound* **11a** as yellow needles (0.100 g, 0.340 mmol, 68%); mp 52–55 °C (decomp.) [Found: *m/z* 295.0090. C₁₁H₁₅FeO₄Si (MH) requires 295.0089]; *v*_{max}(hexane)/cm⁻¹ 2061vs, 2000vs and 1992vs (C=O), 1794s (C=O); δ_{H} (270 MHz) 0.20 (9 H, s, SiMe₃), 1.18 (1 H, d, *J* 11.0, C-5), 1.83 (3 H, s, Me) and 5.76 (1 H, d, *J* 11.0, C-4); δ_{C} {¹H} (67.8 MHz) –0.3 (SiMe₃), 14.2 (Me), 49.8 (C-5), 51.2 (C-3), 104.4 (C-4), 208.3 (C=O) and 235.0 (C-2); *m/z* (FAB, NBA) 294 (M⁺, 29%), 266 (M – CO, 100), 238 (M – 2CO, 76) and 210 (M – 3CO, 47).

4-*tert*-Butyldimethylsilyl-4-phenylsulfonylbutan-2-one ethylene acetal **4b**

A THF solution (50 cm³) of compound **3** (2.56 g, 10.0 mmol) and DMPU (2.70 cm³, 2.86 g, 22.3 mmol) was cooled to –78 °C under an atmosphere of nitrogen. Butyllithium (2.4 mol dm⁻³; 6.0 cm³, 14.4 mmol) was added dropwise to the solution which was then stirred at –78 °C for a further hour. After the reaction had been quenched by addition of *tert*-butyldimethylchlorosilane (1.51 g, 10.0 mmol) to the mixture it was stirred for a further hour at –78 °C and then finally for 1 h at room temperature. Work-up, chromatography and crystallisation as described for compound **4a** gave white crystals of the *title compound* **4b** (3.05 g, 8.24 mmol, 82%); mp 105–106 °C (Found: C 58.1; H, 8.1. C₁₈H₃₁O₄SSi requires C, 58.34; H, 8.16%); *v*_{max}(Nujol)/cm⁻¹ 1297s and 1140vs (SO₂), 1256m and 845m (C-Si); δ_{H} 0.25 (3 H, s, SiMe), 0.39 (3 H, s, SiMe), 0.92 (3 H, s, Me), 1.06 (9 H, s, Bu^t), 2.23 [2 H, d, *J* 4.1, PhSO₂CH(Bu^t-Me₂Si)CH₂], 2.94 [1 H, t, *J* 4.1, PhSO₂CH(Bu^t-Me₂Si)CH₂], 3.64 (4 H, m, OCH₂CH₂O), 7.53 (3 H, m, Ph) and 7.85 (2 H, m, Ph); δ_{C} (67.8 MHz) –3.9 (SiMe), –3.8 (SiMe), 18.0 [C(Me)₃],

23.8 (Me), 27.5 [C(Me)₃], 35.4 (PhSO₂CHCH₂), 49.0 (PhSO₂CHCH₂), 64.1 and 64.2 (OCH₂CH₂O), 108.4 (C-2), 128.3 (C_{ortho} or C_{meta}), 128.5 (C_{ortho} or C_{meta}), 132.7 (C_{para}) and 141.7 (C_{ipso}); *m/z* (CI, NH₃) 371 [(M + H)⁺, 62%] and 229 (M - PhSO₂, 100).

4-*tert*-Butyldimethylsilyl-4-phenylsulfonylbutan-2-one 5b

Compound **4b** (1.11 g, 3.00 mmol) was dissolved in 5 mol dm⁻³ HCl (10 cm³) and acetone (10 cm³) and the solution stirred at room temperature for 16 h. Work-up and chromatography as described for compound **5a** followed by crystallisation gave the *title compound 5b* as white crystals (0.841 g, 2.58 mmol, 86%), mp 83–84 °C (Found: C, 58.6; H, 7.9. C₁₆H₂₇O₃Si requires C, 58.85; H, 8.03%); *v*_{max}(Nujol)/cm⁻¹ 1714s (C=O), 1299s and 1113s (SO₂), 1250s and 864s (C-Si); δ_{H} (270 MHz) 0.19 (3 H, s, SiMe), 0.37 (3 H, s, SiMe), 0.97 [9 H, s, C(Me)₃], 1.79 (3 H, s, Me), 2.68 [1 H, dd, *J* 19.5, 2.5, PhSO₂CH(Bu^tMe₂Si)CH₂], 2.87 [1 H, dd, *J* 19.5, 4.5, PhSO₂CH(Bu^tMe₂Si)CH₂], 3.76 [1 H, dd, *J* 4.5, 2.5, PhSO₂CH(Bu^tMe₂Si)CH₂], 7.40 (3 H, m, Ph) and 7.81 (2 H, m, Ph); δ_{C} {¹H} (67.8 MHz) -6.1 (SiMe), -5.1 (SiMe), 17.4 [C(Me)₃], 26.2 [C(Me)₃], 28.7 (Me), 40.1 [PhSO₂CH(Bu^tMe₂Si)CH₂], 46.6 [PhSO₂CH(Bu^tMe₂Si)CH₂], 127.8 (C_{ortho} or C_{meta}), 128.5 (C_{ortho} or C_{meta}), 132.7 (C_{para}), 139.7 (C_{ipso}) and 202.7 (C=O); *m/z* (CI, NH₃) 327 [(M + H)⁺, 78%] and 127 (C₆H₁₁Osi, 100).

4-*tert*-Butyldimethylsilylbut-3-en-2-one 6b

Compound **5b** (0.328 g, 1.01 mmol) and DBU (0.32 cm³, 0.314 g, 2.12 mmol) were heated to reflux in dichloromethane (5 cm³) under an atmosphere of nitrogen for 1 h. Chromatography as described for **6a** gave compound **6b** as a colourless oil (0.183 g, 0.995 mmol, 99%) [Found: *m/z* 185.1360. C₁₀H₂₁Osi (MH) requires 185.1362]; *v*_{max}(neat)/cm⁻¹ 1681s (C=O), 1592w (C=C), 1253s and 832s (C-Si); δ_{H} (270 MHz) 0.10 (6 H, s, SiMe₂), 0.90 (9 H, s, Bu^t), 2.29 (3 H, s, Me), 6.47 (1 H, d, *J* 19.3 Bu^tMe₂SiCHCH), and 7.04 (1 H, d, *J* 19.3, Bu^tMe₂SiCHCH); δ_{C} {¹H} (67.8 MHz) -6.5 (SiMe₂), 16.5 (CMe₃), 26.3 (CMe₃ and Me), 144.3 (Bu^tMe₂SiCHCH), 145.4 (Bu^tMe₂SiCHCH) and 193.3 (C=O); *m/z* (CI, NH₃) 185 [(M + H)⁺, 100%].

4-Dimethylphenylsilyl-4-phenylsulfonylbutan-2-one ethylene acetal 4c

A THF solution (50 cm³) of compound **3** (2.56 g, 10.0 mmol) and DMPU (2.70 cm³, 2.86 g, 22.3 mmol) was cooled to -78 °C under an atmosphere of nitrogen. Butyllithium (2.4 mol dm⁻³, 4.6 cm³, 11.0 mmol) was added dropwise to the solution which was then stirred at -78 °C for a further hour. The reaction was then quenched by addition of dimethylphenylsilyl chloride (1.71 g, 10.0 mmol) to the mixture which was then stirred for a further hour at -78 °C and finally for 1 h at room temperature. Work-up and chromatography as described for **4a** followed by crystallisation from hexane gave white crystals of the *title compound 4c* (2.56 g, 6.56 mmol, 66%), mp 84–85 °C (Found: C, 61.3; H, 6.6. C₁₈H₃₃O₄Si requires C, 61.51; H, 6.71%); *v*_{max}(Nujol)/cm⁻¹ 1301m and 1140s (SO₂), 1253m and 845m (C-Si); δ_{H} (270 MHz) 0.65 (3 H, s, SiMe), 0.68 (3 H, s, SiMe), 0.78 (3 H, s, Me), 2.12 [1 H, dd, *J* 15.9, 5.1, PhMe₂SiCH(SO₂Ph)CH₂], 2.14 [1 H, dd, *J* 15.9, 3.9, PhMe₂SiCH(SO₂Ph)CH₂], 3.07 [1 H, dd, *J* 5.1, 3.9, PhMe₂SiCH(SO₂Ph)], 3.21 (2 H, m, OCH₂CH₂O), 3.42 (2 H, m, OCH₂CH₂O), 7.63 (3 H, m, Ph) and 7.81 (2 H, m, Ph); δ_{C} (67.8 MHz) -2.5 (SiMe), -1.3 (SiMe), 23.6 (Me), 35.0 (PhSO₂CHCH₂), 51.8 (PhSO₂CHCH₂), 64.3 (OCH₂CH₂O), 108.4 (C-2), 127.8 (C_{ortho} or C_{meta}), 128.3 (C_{ortho} or C_{meta}), 128.7 (C_{ortho} or C_{meta}), 129.6 (C_{para}), 132.8 (C_{para}), 134.5 (C_{ortho} or C_{meta}), 136.7 (C_{ipso}) and 141.3 (C_{ipso}); *m/z* (CI, NH₃) 408 [(M + NH₄)⁺, 10%] and 171 (C₈H₁₅O₂Si, 100).

4-Dimethylphenylsilyl-4-phenylsulfonylbutan-2-one 5c

Compound **4c** (1.10 g, 2.82 mmol) was dissolved in 5 mol dm⁻³ HCl (10 cm³) and acetone (10 cm³) and the solution stirred at room temperature for 16 h. Work-up and chromatography as described for **5a** gave the *title compound 5c* as white crystals (0.949 g, 2.74 mmol, 97%), mp 75–77 °C; *v*_{max}(Nujol)/cm⁻¹ 1714s (C=O), 1299s and 1116s (SO₂), 1252s and 843s (C-Si); δ_{H} (270 MHz) 0.64 (3 H, s, SiMe), 0.65 (3 H, s, SiMe), 1.63 (3 H, s, Me), 2.53 [1 H, dd, *J* 19.0, 5.5, PhMe₂SiCH(SO₂Ph)CH₂], 2.80 [1 H, dd, *J* 19.0, 5.5, PhMe₂SiCH(SO₂Ph)CH₂], 3.82 (1 H, t, *J* 5.5, PhSO₂CH) and 7.53 (10 H, m, Ph); δ_{C} {¹H} (67.8 MHz) -3.5 (SiMe), -1.7 (SiMe), 29.2 (Me), 39.9 (C-3), 50.2 (C-4), 127.9 (C_{ortho} or C_{meta}), 128.1 (C_{ortho} or C_{meta}), 129.0 (C_{ortho} or C_{meta}), 129.9 (C_{para}), 133.2 (C_{para}), 134.4 (C_{ortho} or C_{meta}), 135.0 (C_{ipso}), 140.5 (C_{ipso}) and 203.5 (C=O); *m/z* 364 [(M + NH₄)⁺, 30%] and 127 (C₆H₁₁Osi, 100).

4-Dimethylphenylsilylbut-3-en-2-one 6c¹⁴

Compound **5c** (0.360 g, 1.04 mmol) and DBU (0.34 cm³, 0.346 g, 2.28 mmol) were heated to reflux in dichloromethane (5 cm³) under an atmosphere of nitrogen for 1 h. Chromatography as described for **6a** gave **6c** as a colourless oil (0.125 g, 0.613 mmol, 59%) [Found: *m/z* 205.1050. C₁₂H₁₇Osi (MH) requires 205.1049]; *v*_{max}(neat)/cm⁻¹ 1679s (C=O), 1591w (C=C), 1253m and 829s (C-Si); δ_{H} (270 MHz) 0.45 (6 H, s, SiMe₂), 2.29 (3 H, s, Me), 6.48 (1 H, d, *J* 19.3, PhMeSiCHCH), 7.12 (1 H, d, *J* 19.3, PhMeSiCHCH), 7.38 (3 H, m, Ph) and 7.52 (2 H, m, Ph); δ_{C} {¹H} (67.8 MHz) -3.2 (SiMe₂), 26.3 (Me), 128.0 (C_{ortho} or C_{meta} or C_{para}), 129.6 (C_{ortho} or C_{meta} or C_{para}), 133.8 (C_{ortho} or C_{meta} or C_{para}), 136.3 (C_{ipso}), 144.1 (PhMe₂SiCHCH), 145.4 (PhMe₂SiCHCH) and 198.4 (C=O); *m/z* (CI, NH₃) 205 [(M + H)⁺, 22%] and 44 (MeSiH, 100).

Tetracarbonyl(4-*tert*-butyldimethylsilylbut-3-en-2-one)iron(0) 7b

Compound **6b** (0.284 g, 1.54 mmol) and [Fe₂(CO)₉] (1.30 g, 3.57 mmol) were heated in diethyl ether (15 cm³) at 35 °C for 14 h under an atmosphere of nitrogen. Filtration, solvent removal and chromatography as described for **7a** gave the *title compound 7b* as an orange oil (0.337 g, 0.957 mmol, 62%) [Found: *m/z* 353.0510. C₁₄H₂₁FeO₅Si (MH) requires 353.0508]; *v*_{max}(hexane)/cm⁻¹ 2096vs, 2034vs, 2012vs and 1993vs (C=O), 1682w (C=O), 1252w and 825w (C-Si); δ_{H} (270 MHz) -0.12 (3 H, s, SiMe), 0.23 (3 H, s, SiMe), 0.95 (9 H, s, Bu^t), 2.37 (3 H, s, Me), 2.72 (1 H, d, *J* 13.2, C-3) and 3.42 (1 H, d, *J* 13.2, C-4); δ_{C} {¹H} (125.8 MHz) -6.9 (SiMe), -3.3 (SiMe), 18.2 [C(Me)₃], 26.5 [C(Me)₃], 29.1 (Me), 40.0 (C-3), 59.9 (C-4), 203.0 (C=O) and 208.1 (C=O); *m/z* (FAB) 353 [(M + H)⁺, 27%], 325 (M + H - CO, 32), 296 (M - 2CO, 37), 268 (M - 3CO, 54), 240 (M - 4CO, 38) and 55 (C₄H₇, 100).

Tricarbonyl(4-*tert*-butyldimethylsilylbut-3-en-2-one)iron(0) 8b

Compound **6b** (0.284 g, 1.54 mmol) and [Fe₂(CO)₉] (1.30 g, 3.57 mmol) were heated in toluene (15 cm³) at 55 °C for 14 h under an atmosphere of nitrogen. Filtration, solvent removal and chromatography as described for compound **8a** gave the *title compound 8b* as an orange oil (0.380 g, 1.17 mmol, 76%) [Found: *m/z* 325.0560. C₁₃H₂₁FeO₄Si (MH) requires 325.0562]; *v*_{max}(hexane)/cm⁻¹ 2069vs, 2009vs and 1982vs (C=O), 1259m and 826m (C-Si); δ_{H} (270 MHz) -0.06 (3 H, s, SiMe), 0.14 (3 H, s, SiMe), 0.92 (9 H, s, Bu^t), 1.13 (1 H, d, *J* 11.0, Bu^tMe₂SiCHCH), 2.51 (3 H, s, Me) and 5.60 (1 H, d, *J* 11.0, Bu^tMe₂SiCHCH); δ_{C} (67.8 MHz) -7.13 (SiMe), -3.87 (SiMe), 17.4 [C(Me)₃], 20.9 (Me), 26.5 [C(Me)₃], 46.9 [Bu^tMe₂SiCHCH(O)Me], 85.9 [Bu^tMe₂SiCHCH(O)Me], 143.8 (C=O), 203.9 (C=O) and 210.5 (C=O); *m/z* (EI) 324 (M⁺, 0.2%), 296 (M - CO, 0.2), 268 (M - 2CO, 0.6), 240 (M - 3CO, 0.5) and 127 (C₆H₁₁Osi, 100).

Tetracarbonyl(4-dimethylphenylsilylbut-3-en-2-one)iron(0) 7c

Compound **6c** (0.102 g, 0.500 mmol) and $[\text{Fe}_2(\text{CO})_9]$ (0.73 g, 2.01 mmol) were heated in diethyl ether (15 cm³) at 35 °C for 14 h under an atmosphere of nitrogen. Filtration, solvent removal and chromatography as described for compound **7a** gave the *title compound 7c* as an orange oil (0.086 g, 0.230 mmol, 46%); $\nu_{\text{max}}(\text{hexane})/\text{cm}^{-1}$ 2096vs, 2034vs, 2013vs and 1993vs (C≡O), 1682w (C=O), 1252w and 825w (C-Si); $\delta_{\text{H}}(270 \text{ MHz})$ 0.42 (3 H, s, SiMe), 0.47 (3 H, s, SiMe), 2.40 (3 H, s, Me), 2.95 (1 H, d, *J* 13.2, C-3), 3.53 (1 H, d, *J* 13.2, C-4), 7.39 (3 H, m, Ph) and 7.54 (2 H, m, Ph); $\delta_{\text{C}}\{^1\text{H}\}$ (125.8 MHz) -1.5 (SiMe), -0.6 (SiMe), 29.1 (Me), 41.2 (C-3), 59.2 (C-4), 203.0 (C=O) and 207.6 (C≡O).

Tricarbonyl(4-dimethylphenylsilylbut-3-en-2-one)iron(0) 8c

Compound **6c** (0.071 g, 0.348 mmol) and $[\text{Fe}_2(\text{CO})_9]$ (0.260 g, 0.714 mmol) were heated in toluene (15 cm³) at 55 °C for 14 h under an atmosphere of nitrogen. Filtration, solvent removal and chromatography as described for **8a** gave the *title compound 8c* as an orange oil (0.038 g, 0.110 mmol, 32%); $\nu_{\text{max}}(\text{hexane})/\text{cm}^{-1}$ 2070vs, 2010vs and 1983vs (C≡O), 1252m and 826m (C-Si); $\delta_{\text{H}}(270 \text{ MHz})$ -2.5 (3 H, s, SiMe), 1.40 (3 H, s, SiMe), 0.87 (1 H, d, *J* 10.7, PhMe₂SiCHCH), 2.51 (3 H, s, Me), 5.62 (1 H, d, *J* 10.7, PhMe₂SiCHCH), 7.36 (3 H, m, Ph) and 7.54 (2 H, m, Ph); $\delta_{\text{C}}\{^1\text{H}\}$ (67.8 MHz) -2.15 (SiMe), -1.40 (SiMe), 20.8 (Me), 48.1 [PhMe₂SiCHCHC(O)Me], 85.0 [PhMe₂SiCHCHC(O)Me], 127.9 (*C*_{ortho} or *C*_{meta}), 129.3 (*C*_{para}), 133.7 (*C*_{ortho} or *C*_{meta}), 144.1 (*C*_{ipso}), 145.7 (C=O) and 208.2 (C≡O).

3-tert-Butyldimethylsilylhexane-2,5-dione 10

A solution of compound **8b** (0.090 g, 0.278 mmol) in THF (15 cm³) was cooled to -78 °C and methyllithium (1.5 mol dm⁻³; 0.23 cm³, 0.345 mmol) was added dropwise to it. The solution was stirred first at -78 °C for 30 min and then at room temperature for 30 min after which the resulting dark red solution was cooled to -78 °C and quenched with Bu^tBr (0.10 cm³, 0.119 g, 0.869 mmol). Work-up and chromatography as described for compound **9** gave the *title compound 10* as a colourless oil (0.0245 g, 0.107 mmol, 38%) [Found: *m/z* 229.1635. C₁₂H₂₄O₂Si (MH) requires 229.1624]; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 1720s (C=O), 1692s (C=O), 1253m and 824m (C-Si); $\delta_{\text{H}}(270 \text{ MHz})$ 0.01 (3 H, s, SiMe), 0.06 (3 H, s, SiMe), 0.92 (9 H, s, Bu^t), 2.11 (3 H, s, Me), 2.21 (3 H, s, Me), 2.43 [1 H, dd, *J* 18.3, 1.9, CH₃C(O)CH(Bu^tMe₂Si)CH₂], 2.97 [1 H, dd, *J* 11.7, 1.9, CH₃C(O)CH(Bu^tMe₂Si)CH₂] and 3.15 [1 H, dd, *J* 18.3, 11.7, CH₃C(O)CH(Bu^tMe₂Si)CH₂]; $\delta_{\text{C}}(67.8 \text{ MHz})$ -6.6 (SiMe), -5.9 (SiMe), 17.9 [C(Me)₃], 26.8 [C(Me)₃], 29.6 and 32.2 (2 × Me), 39.3 and 42.8 [CH₃C(O)CH(Bu^tMe₂Si)CH₂], 207.4 and 210.3 (2 × C=O); *m/z* (EI) 229 [(M + H)⁺, 0.1%] 185 (M - CH₃CO, 1.3) and 75 (C₂H₇OSi, 100).

Tricarbonyl(5-tert-butyldimethylsilyl-3-methyl-1-oxapenta-1,2,4-triene)iron(0) 11b

Compound **8b** (0.052 g, 0.160 mmol) was dissolved in THF (15 cm³) and the solution cooled to -78 °C whilst being continually purged with carbon monoxide. Methyllithium (1.44 mol dm⁻³; 0.76 cm³, 1.09 mmol) was added dropwise to the reaction mixture which was then stirred at -78 °C for 40 min.

Work-up and chromatography as described for compound **11a** and crystallisation gave the *title compound 11b* as yellow needles (0.028 g, 0.0833 mmol, 52%), mp 73–76 °C (decomp.) (Found: C, 49.7; H, 6.1. C₁₄H₂₀FeO₄Si requires C, 49.96; H, 6.01%); $\nu_{\text{max}}(\text{hexane})/\text{cm}^{-1}$ 2061vs, 2000vs and 1992vs (C≡O) and 1794m (C=O); $\delta_{\text{H}}(270 \text{ MHz})$ 0.14 (3 H, s, SiMe), 0.16 (3 H, s, SiMe), 0.93 (9 H, s, Bu^t), 1.22 (1 H, d, *J* 11.2, Bu^tMe₂SiCHCH), 1.84 (3 H, s, Me) and 5.75 (1 H, d, *J* 11.2, Bu^tMe₂SiCHCH); $\delta_{\text{C}}\{^1\text{H}\}$ (67.8 MHz) -7.8 (SiMe), -3.5 (SiMe), 14.3 (Me), 17.5 [C(CH₃)₃], 26.5 [C(CH₃)₃], 46.9 (C-4), 51.2 (C-5), 105.2 (C-3), 208.0 (C≡O) and 235.2 (C-2); *m/z* (EI) 336 (M⁺, 0.3%), 308 (M - CO, 0.5), 280 (M - 2CO, 0.7), 252 (M - 3CO, 1.6), 224 (M - 4CO, 2.8) and 111 (C₆H₁₁Si, 100).

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