A new synthesis of iron(0) vinylketene complexes

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Reaction of vinyllithium reagents generated from vinylstannanes [(*E*)-RCH=CHSnBu$_3$ (R = Ph, SiPh$_3$, SiMe$_3$, *n*-C$_5$H$_{11}$), 1a–d] with [Fe(CO)$_4$L] (L = CO, PPh$_3$) followed by an ethyl trifluoromethanesulfonate quench gives vinylketene complexes [Fe^0(CO)$_2$L{RCH=CHC(OEt)C=O}] 2a–f, in a one-pot reaction sequence in 31–55% yield.

The chemistry of transition-metal complexes of vinylketenes is of both synthetic and mechanistic interest, as (*i*) they may be regarded as stable, synthetically malleable forms of normally transient vinylketenes,[1] and (*ii*) they are thought to be key intermediates in a variety of transition-metal mediated organic reactions that give rise to a diverse range of organic products.[2] Iron carbonyl based vinylketene complexes, which have been the subject of the majority of the reactivity studies to date, have been synthesised by several methods: reaction of cyclopropenes with [Fe$_2$(CO)$_9$],[3] reaction of allyl halides with [Fe$_2$(CO)$_9$],[4] reaction of iron tricarbonyl complexes of α,β-unsaturated ketones with methyllithium under a carbon monoxide atmosphere,[5] and carbonylation of vinylcarbene complexes formed either by (*i*) reaction of [Fe(CO)$_4$]$^{2-}$ with α,β-unsaturated acid chlorides followed by *O*-acylation or *O*-alkylation,[6] or by (*ii*) hydrometallation of electron-deficient alkynes with [HFe(CO)$_4$]$^-$ followed by *O*-alkylation.[7] In view of the current interest in metal-coordinated vinylketenes, we wish to communicate herein a new, relatively efficient and relatively versatile method for the synthesis of iron carbonyl complexes of vinylketenes.

Drawing on the observation that iron alkynylcarbene complexes, formed by adding alkynyllithiums to [Fe(CO)$_5$] and quenching with ethyl fluorosulfonate, undergo [4 + 2] cycloadditions with cyclopentadiene to give vinylcarbene complexes which readily convert to vinylketene complexes at room temperature,[8] we postulated that addition of vinyllithium reagents to [Fe(CO)$_5$] followed by addition of a hard electrophile should provide direct access to vinylketene complexes. Accordingly, *trans*-1-phenyl-2-(tri-*n*-butylstannyl)ethene **1a** was synthesised by heating 1-phenylethyne with tri-*n*-butyltin hydride.† Transmetallation of **1a** using *n*-butyllithium in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmen) gave the corresponding vinyllithium reagent which was treated *in situ* with [Fe(CO)$_5$]. Addition of hexamethylphosphoramide (HMPA) to the reaction mixture followed by ethyl trifluoromethanesulfonate and subsequent work-up gave a red oil which on chromatography and crystallisation produced air-stable amber crystals. Examination of the spectroscopic and analytical data of these revealed that they were indeed the anticipated vinylketene complex **2a**, formed in what may be regarded as a good yield from vinylstannane **1a** (46%) (Table 1, entry 1) when due consideration is given to the number of bonds being formed in the one-pot reaction sequence.‡ It is also worthy of comment that the conversion of vinylstannane **1a** into the vinylketene complex **2a** results in the 'fixation' of two molecules of carbon monoxide to the vinyl residue derived from the stannane.

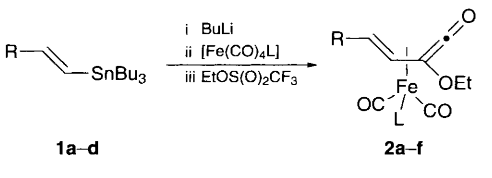
In principle, addition of vinyllithium reagents to phosphine derivatives of [Fe(CO)$_5$] should provide ready access to a range of phosphine-substituted vinylketene complexes. In order to test this hypothesis, stannane **1a** was transmetallated using *n*-butyllithium and added to [Fe(CO)$_4$(PPh$_3$)]. Pleasingly, quenching with ethyl trifluoromethanesulfonate and work-up gave the novel§ triphenylphosphine substituted vinylketene complex **2b** as air-stable yellow crystals in 42% yield (Table 1, entry 2).

In order to further demonstrate the relative versatility of this new approach to iron vinylketene complexes, several other

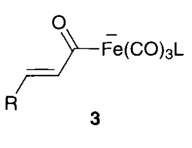
Table 1 Synthesis of vinylketene complexes **2a–f** from vinylstannanes **1a–d**[a]

Entry	vinyl-stannane	R	L	vinylketene complex	yield (%)
1	**1a**	Ph	CO	**2a**	46
2	**1a**	Ph	PPh$_3$	**2b**	42
3	**1b**	SiPh$_3$	CO	**2c**	31
4	**1c**	SiMe$_3$	PPh$_3$	**2d**	55
5	**1d**	*n*-C$_5$H$_{11}$	CO	**2e**	54
6	**1d**	*n*-C$_5$H$_{11}$	PPh$_3$	**2f**	31

[a] The procedure used for the synthesis of tricarbonyl(3-ethoxy-5-phenyl-1-oxapentatriene)iron(0) **2a** is typical: *n*-Butyllithium (1.47 mol dm^{-3}, 1.70 cm^3, 2.50 mmol) was added dropwise to a solution of *trans*-1-phenyl-2-(tri-*n*-butylstannyl)ethene **1a** (0.786 g, 2.00 mmol) and tmen (0.38 cm^3, 2.5 mmol) under nitrogen in dry diethyl ether 5 cm^3) at −78 °C. The resultant cherry red solution was warmed immediately to −30 °C, stirred for 1 h, allowed to warm to −10 °C over 30 min and then recooled to −78 °C. Dropwise addition of dry [Fe(CO)$_5$] (0.53 cm^3, 2.5 mmol) resulted in the precipitation of an oily red solid and the supernatant becoming deep red. Allowing the solution to warm to room temp. over 3.5 h led to a homogeneous solution. Dry HMPA (2.5 cm^3) in dry diethyl ether (5 cm^3) was added, and after purging the reaction vessel thoroughly with carbon monoxide, the reaction mixture was again cooled to −78 °C. Ethyl trifluoromethanesulfonate (1.62 cm^3, 12.5 mmol) was added dropwise and the deep red solution was allowed to warm to room temp. overnight. The milky orange-brown mixture was extracted with diethyl ether (50 cm^3) and the organic phase washed with saturated aqueous NaHCO$_3$ (2 × 50 cm^3) and brine (50 cm^3) and then dried (Na$_2$SO$_4$). Concentration, filtration (Al$_2$O$_3$; diethyl ether) and removal of the solvent from the filtrate under reduced pressure yielded a red oil. Chromatography [SiO$_2$; light petroleum (b.p. 40–60 °C)–Et$_2$O, 98:2 to 90:10, gradient elution] followed by recrystallisation from diethyl ether–light petroleum (b.p. 60–80 °C) gave tricarbonyl(3-ethoxy-5-phenyl-1-oxapentatriene)iron(0) **2a** (0.299 g, 0.91 mmol, 46%) as amber crystals.



1a–d **2a–f**



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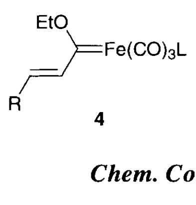

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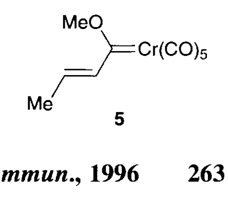

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vinylstannanes were synthesised from terminal alkynes, transmetallated and added to [Fe(CO)$_5$] or [Fe(CO$_4$)(PPh$_3$)]. Thus, addition of vinyllithium reagents derived from (triphenylsilyl)ethyne and (trimethylsilyl)ethyne *via* the silyl-substituted stannanes **1b** and **1c**, to [Fe(CO)$_5$] and [Fe(CO)$_4$(PPh$_3$)] respectively, gave the novel silyl-substituted vinylketene complexes **2c** and **2d** (Table 1, entries 3 and 4). Similarly conversion of hept-1-yne into vinylstannane **1d**,¶ transmetallation and addition to [Fe(CO)$_5$] and [Fe(CO)$_4$(PPh$_3$)] gave the novel alkyl-substituted vinylketene complexes **2e** and **2f** respectively (Table 1, entries 5 and 6).

It is postulated that the synthesis of vinylketene complexes described above proceeds by addition of the vinyllithium reagents to [Fe(CO$_4$)L] (L = CO, PPh$_3$) to give the anionic intermediates **3**. Quenching with ethyl trifluoromethanesulfonate provides iron carbenes **4** which on insertion of carbon monoxide into the iron–carbon double bond and subsequent carbon–carbon double bond coordination give the products **2a–f**. It is of interest to compare this process with the addition of *trans*-1-lithioprop-1-ene to [Cr(CO)$_6$] followed by quenching with methyl fluorosulfonate.[10] This reaction sequence leads only to the isolation of chromium vinylcarbene **5** suggesting that the activation energy for the insertion of carbon monoxide into chromium metal–carbon double bonds is higher than for carbon monoxide insertion into iron–carbon double bonds.

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Footnotes

† Stannanes **1a–d** were synthesized in 93, 68, 94 and 95% yield respectively by heating tri-*n*-butyltin hydride with the appropriate terminal alkyne at 100–150 °C for 48 h.[9]

‡ For comparison, reaction of [Fe(CO)$_4$]$^{2-}$ {formed from [Fe(CO)$_5$] and K(BHBu$^{s}{}_{3}$)} with cinnamoyl chloride followed by ethyl fluorosulfonate gave the vinylketene complex **2a** in 14% yield.[6]

§ The previously reported vinylketene complex **2a**[6] and the novel complexes **2b–f** gave satisfactory IR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, low-resolution mass spectral and microanalytical/high resolution mass spectral data.

¶ Stannane **1d** was formed as a 4:1 mixture of *trans*-1-(tri-*n*-butylstannyl)hept-1-ene and 2-(tri-*n*-butylstannyl)hept-1-ene and used without further purification; the yields quoted for vinylketene complexes **2e** and **2f**, however, are for isomerically pure material.

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