Nucleophilic Addition to Vinylketene- and Vinylketenimine (Allenylideneamine)-tricarbonyliron(0) Complexes

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Nucleophiles add to C-1 of (vinylketene)tricarbonyliron(0) complexes to give β,γ-unsaturated carbonyl derivatives, whereas nucleophilic attack on a (vinylketenimine)tricarbonyliron(0) analogue occurs at C-2 and leads, after an oxidative work-up, to β,γ-unsaturated amides containing an α quaternary centre.

We have recently discovered novel routes to (vinylketene)tricarbonyliron(0) and (vinylketenimine)tricarbonyliron(0) (vinylketenimine = allenylideneamine) complexes which makes these stable crystalline derivatives of highly reactive unstable organic molecules readily available from simple starting materials.[1-3] As part of a series of investigations into the general reactivity of the complexes, we have examined their reactions with nucleophiles for the first time.[4] In this communication we report the results of these studies which

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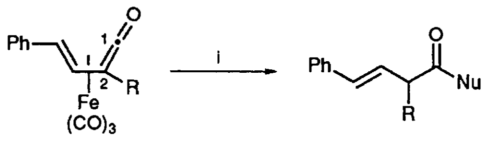
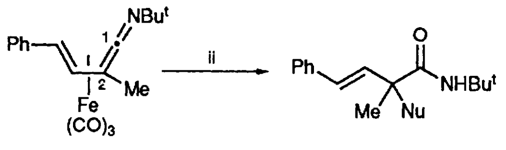


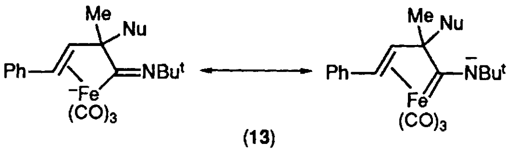
(1) R = Me
(2) R = Bu^t

(3) R = Me, Nu = Me
(4) R = Me, Nu = CMe_2CO_2Et
(5) R = Bu^t, Nu = $NHCH_2Ph$
(6) R = Bu^t, Nu = OMe
(7) R = Bu^t, Nu = SBu^t



(8)

(9) Nu = Me
(10) Nu = Et
(11) Nu = Bu^n
(12) Nu = Bu^t



(13)

Reagents: i, NuLi, NuNa, or NuH, then Bu^tBr or AcOH; ii, NuLi, then Bu^tBr, then air oxidation.

Table 1. Addition of nucleophiles to (vinylketene)tricarbonyliron(0) and (vinylketenimine)tricarbonyliron(0) complexes.[a]

Entry	Complex	NuLi, NuNa, NuH	Product[b]	% Yield[c]
1	**(1)**	MeLi	**(3)**	71
2	**(1)**	$LiCMe_2CO_2Et$	**(4)**	67
3	**(2)**	$PhCH_2NH_2$	**(5)**	85
4	**(2)**	NaOMe	**(6)**	89
5	**(2)**	Bu^tSNa	**(7)**	74
6	**(8)**	MeLi	**(9)**	53
7	**(8)**	EtLi	**(10)**	54
8	**(8)**	Bu^nLi	**(11)**	57
9	**(8)**	Bu^tLi	**(12)**	63

[a] *Entries 1—5* typically involved stirring the vinylketene complex (0.3 mmol) and the nucleophile (1.1 equiv.) in tetrahydrofuran (THF) under a nitrogen atmosphere either at −78 °C for 2 h (entries 1 and 2) or at room temperature for 16 h (entries 3—5). The reaction mixture was quenched with either Bu^tBr (entries 1, 2) or acetic acid (entries 3—5), and allowed to warm to room temperature if appropriate. *Entries 6—9* typically involved stirring the vinylketenimine complex (0.1—0.4 mmol) and the nucleophile (1.1 equiv.) at −78 °C for 1—4 h in THF under a nitrogen atmosphere. The reaction mixture was quenched with Bu^tBr, allowed to warm to room temperature, and filtered through Al_2O_3. The filtrate was concentrated *in vacuo*, dissolved in $CHCl_3$, and stirred overnight under air. [b] All products gave satisfactory IR, ^1H NMR, low resolution mass spectral and microanalytical/high resolution mass spectral data. [c] Yields refer to purified products isolated by column chromatography.

reveal that nucleophilic attack on vinylketene complexes occurs at C-1 and leads to β,γ-unsaturated carbonyl derivatives whereas nucleophilic attack on a vinylketenimine analogue occurs at C-2 and produces on work-up β,γ-unsaturated amides containing an α quaternary centre.

Initially the reactivity of (vinylketene)tricarbonyliron(0) complexes towards nucleophiles was examined. Carbon, nitrogen, oxygen, and sulphur nucleophiles were found to react with vinylketene complexes (**1**)[1,3] and (**2**)[1,3] to give products identified as the novel α-alkyl-β,γ-unsaturated carbonyl compounds (**3**)—(**7**) (Table 1, entries 1—5). Thus nucleophilic attack occurs at C-1 of complexes (**1**) and (**2**) and the reactivity of the metal-bound vinylketenes towards nucleophiles parallels both the characteristic and well documented C-1 addition of nucleophiles to free ketenes,[5] and the relatively unstudied C-1 addition of nucleophiles to free vinylketenes.[6]

The first reaction between a (vinylketenimine)tricarbonyliron(0) complex and a nucleophile to be investigated was the addition of methyl-lithium to complex (**8**).[2,3] Quenching the reaction mixture with t-butyl bromide gave rise to an unstable organometallic complex which after aerial oxidation and chromatography produced a pure organic product identified as the novel α,α-dialkyl-β,γ-unsaturated amide (**9**) (Table 1, entry 6). Similarly addition of ethyl-lithium, n-butyl-lithium, and t-butyl-lithium to vinylketenimine complex (**8**) gave novel unsaturated amides (**10**), (**11**), and (**12**) (Table 1, entries 7—9). [It is of note that amide (**12**) contains two contiguous quaternary centres.] Attempts to add oxygen, nitrogen, or sulphur nucleophiles to compound (**8**) led to either complex mixtures of products or isolation of unchanged starting material.

The structures of products (**9**)—(**12**) reveal that in contrast to nucleophilic attack on free ketenimines which has been observed to occur at C-1,[7] nucleophilic attack on the (vinylketenimine)tricarbonyliron(0) complex (**8**) occurs at C-2.[8] It is proposed that the initial adducts in the reaction between complex (**8**) and the alkyl-lithium reagents are the anions (**13**) which after protonation on nitrogen give allyl aminocarbene complexes. These unstable intermediates are then oxidised to the α,α-dialkyl-β,γ-unsaturated amides (**9**)—(**12**).

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