Conversion of (Vinylketene)tricarbonyliron(0) Complexes to (Vinylketenimine)tricarbonyliron(0) Complexes

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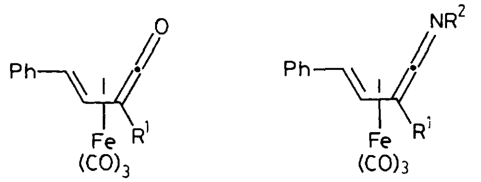
Heating (vinylketene)tricarbonyliron(0) complexes with isonitriles at 80 °C gives (vinylketenimine)tricarbonyliron(0) complexes *via* intermediate (vinylketene)dicarbonylisonitrileiron(0) complexes.

The reactivity of co-ordinated vinylketene ligands is a relatively neglected area[1] worthy of further investigation in view of the high reactivity of free vinylketenes and ketenes,[2] and the frequent postulation of metal-bound vinylketenes as reaction intermediates.[3] As a result of our interest in the chemistry of (heterodiene)tricarbonyliron(0) complexes, we recently discovered that readily available (vinylketone)tricarbonyliron(0) complexes are conveniently converted into (vinylketene)tricarbonyliron(0) complexes on treatment with organolithium reagents under an atmosphere of carbon monoxide.[4] Our investigations into the reactivity of the (vinylketene)tricarbonyliron(0) complexes have revealed that on heating with an isonitrile the vinylketene ligand is cleanly transformed into a vinylketenimine ligand. This novel transformation and experiments which shed light on the pathway of the reaction are described below.

The (vinylketene)tricarbonyliron(0) complex (**1**) was synthesised from the corresponding (vinylketone)tricarbonyliron(0) complex by stirring with methyl-lithium under an atmosphere of carbon monoxide.[4] Heating complex (**1**) with t-butyl isonitrile at 80 °C in toluene for 10 h (Scheme 1) led to the production of a yellow crystalline air-stable organometallic complex which was identified as the novel (vinylketen-



(**1**) R^1 = Me $\xrightarrow{i}$ (**2**) R^1 = Me, R^2 = Bu^t (64%)

(**1**) $\xrightarrow{ii}$ (**3**) R^1 = Me, R^2 = cyclohexyl (59%)

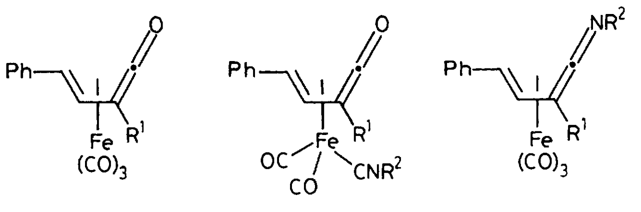
(**1**) $\xrightarrow{iii}$ (**4**) R^1 = Me, R^2 = 2,6-dimethylphenyl (60%)

(**1**) $\xrightarrow{iv}$ (**5**) R^1 = Me, R^2 = CH(Me)Ph (51%)

(**1**) $\xrightarrow{v}$ (**6**) R^1 = Me, R^2 = CH(Me)Bu^t (71%)

(**7**) R^1 = Bu^t $\xrightarrow{vi}$ (**8**) R^1 = Bu^t, R^2 = Bu^t (58%)

Scheme 1. *Reagents and conditions*: i, Bu^tNC, 10 h, 80 °C; ii, $C_6H_{11}NC$, 16 h, 80 °C; iii, $(2,6\text{-}Me_2)C_6H_3NC$, 24 h, 80 °C; iv, PhCH(Me)NC, 18 h, 80 °C; v, $Bu^tCH(Me)NC$, 18 h, 80 °C; vi, Bu^tNC, 24 h, 80 °C. Products (**5**) and (**6**) were obtained as 1:1 mixtures of diastereoisomers.



$(1)\ R^1 = Me \xrightarrow{i} (9)\ R^1 = Me, R^2 = Bu^t\ (25\%) \xrightarrow{ii} (2)\ R^1 = Me, R^2 = Bu^t\ (63\%)$
$[+(2)\ (41\%)]$

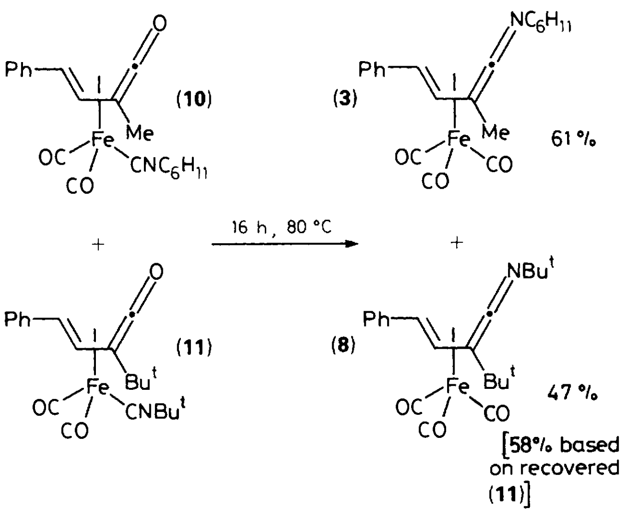
$(1) \xrightarrow{iii} (10)\ R^1 = Me, R^2 = \text{cyclohexyl}\ (35\%) \xrightarrow{iv}$
$[+(3)\ (23\%)]$
$(3)\ R^1 = Me, R^2 = \text{cyclohexyl}\ (68\%)$

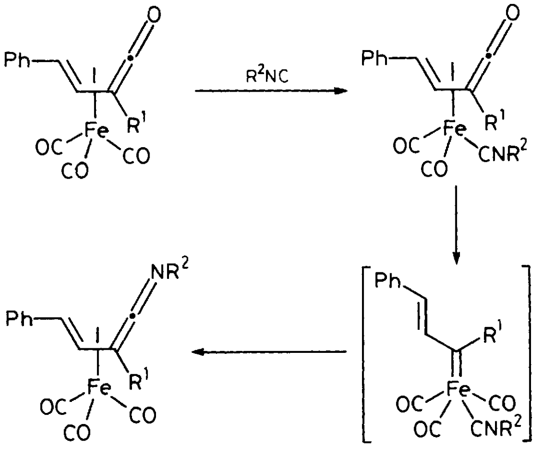
$(7)\ R^1 = Bu^t \xrightarrow{v} (11)\ R^1 = Bu^t, R^2 = Bu^t\ (45\%) \xrightarrow{vi} (8)\ R^1 = Bu^t, R^2 = Bu^t\ (68\%)$
$[+(8)\ (22\%)]$

Scheme 2. *Reagents and conditions*: i, Bu^{t}NC, 3.5 h, 80 °C; ii, 10 h, 80 °C; iii, $C_6H_{11}NC$, 3 h, 80 °C; iv, 16 h, 80 °C; v, Bu^{t}NC, 3 h, 80 °C; vi, 22 h, 80 °C.

imine)tricarbonyliron(0) complex (**2**) by IR, ^1H NMR, ^{13}C NMR, mass spectral, and microanalytical data.† The data were in good agreement with values reported for a related (vinylketenimine)tricarbonyliron(0) complex which had been further characterised by an *X*-ray diffraction study.[5] Similarly complex (**1**) was readily converted into the novel (vinylketenimine)tricarbonyliron(0) complexes (**3**)—(**6**),‡ and (vinylketene)tricarbonyliron(0) complex (**7**)[4] was converted into the novel (vinylketenimine)tricarbonyliron(0) complex (**8**) by heating in toluene with the appropriate isonitrile.

Halting the reaction between (vinylketene)tricarbonyliron(0) complexes and isonitriles after a fraction of the time required to give complete conversion to (vinylketenimine)tricarbonyliron(0) complexes revealed that (vinylketene)dicarbonylisonitrileiron(0) complexes were intermediates in the reaction. For example, heating complex (**1**) with t-butyl isonitrile for 3.5 h gave a mixture of (vinylketenimine)tricarbonyliron(0) (**2**), and (vinylketene)dicarbonylisonitrileiron(0) (**9**) (Scheme 2). Complexes (**2**) and (**9**) were isolated in 41 and 25% yield, respectively, and the novel complex (**9**) was characterised fully.† Heating a pure sample of complex (**9**) converted it cleanly into complex (**2**). Similarly (vinylketene)dicarbonylisonitrileiron(0) complexes (**10**) and (**11**) were shown to be intermediates in the reactions between complex (**1**) and cyclohexyl isonitrile, and complex (**7**) and t-butyl isonitrile, respectively.





Scheme 3

In order to determine whether or not dissociation of the isonitrile ligand from the metal occurs during the conversion of (vinylketene)dicarbonylisonitrileiron(0) complexes to (vinylketenimine)tricarbonyliron(0) complexes, compounds (**10**) and (**11**) were heated together in toluene at 80 °C until complex (**10**) had been consumed. The resulting material contained a mixture of vinylketenimine complexes (**3**) and (**8**) and starting complex (**11**), which were isolated in 61, 47, and 19% yield, respectively. We were unable to detect any evidence for the generation of cross-over products during the experiment, which suggests that the carbonyl/isonitrile exchange process occurs intramolecularly. This result is consistent with an observation made during the course of studies on the ketene complex $(Ph_2C{=}C{=}O)(CO)_3Fe(^0)$.[6] Stirring the diphenylketene complex under a ^{13}CO atmosphere gave material in which the ketene carbonyl and metal carbonyls were equally enriched and a subsequent double labelling experiment demonstrated that the carbonyl exchange process in this complex was intramolecular in nature.

In considering the reaction pathway for the conversion of vinylketene ligands to vinylketenimine ligands, it is of

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† *Analytical data* for (**2**): m.p. 79—79.5 °C; $\nu_{max.}$ (C_6H_{12}) 2040vs, 1982vs, 1978vs (C≡O) and 1720m (C=N) cm^{-1}; NMR δ_H ($CDCl_3$) 1.41 (9H, s, Bu^t), 2.04 (3H, s, Me), 2.88 (1H, d, *J* 9 Hz, -CH=C*H*Ph), 6.14 (1H, d, *J* 9 Hz, -C*H*=CHPh), and 7.2—7.4 (5H, m, Ph); δ_C ($CDCl_3$) 17.3 [Bu^{t}N=C=C(CH$_3$)-], 29.5 [C(CH$_3$)$_3$], 56.4 [C(Me)$_3$], 57.7 [Bu^{t}N=C=C(Me)-], 59.0 (-CH=CHPh), 93.0 (-CH=CHPh), 126.2, 126.9, 128.8, 138.8 (Ph), 183.6 [Bu^{t}N=C=C(Me)-], 205.5, 210.0, and 215.2 (C≡O); FAB MS *m/z* 354 (*M*H$^+$, 66%), 326 (31, *M*H − CO), 297 (18, *M* − 2CO), and 269 (100, *M* − 3CO).

For (**9**): m.p. 64—65 °C; $\nu_{max.}$ (C_6H_{12}) 2145m (C≡NBu^t), 2015vs, 1969vs (C≡O), and 1765br m (C=O); NMR δ_H ($CDCl_3$) 1.36 (9H, s, Bu^t), 1.85 (3H, s, Me), 2.97 (1H, d, *J* 9 Hz, -CH=C*H*Ph), 6.26 (1H, d, *J* 9 Hz, -C*H*=CHPh), and 7.2—7.5 (5H, m, Ph); δ_C ($CDCl_3$) 14.0 [O=C=C(CH$_3$)-], 30.4 [C≡NC(CH$_3$)$_3$], 47.6 [O=C=C(Me)-], 55.0 (-CH=CHPh), 57.2 [C≡NC(Me)$_3$], 97.3 (-CH=CHPh), 125.8, 126.4, 128.4, 140.7 (Ph), 155.6 (C≡NBu^t), 212.7 (2 × C≡O), and 225.1 [O=C=C(Me)-]; FAB MS *m/z* 354 (*M*H$^+$, 17%), 325 (12, *M* − CO), 298 (21, *M*H − 2CO), 269 (100, *M* − 3CO).

‡ The novel complexes (**2**)—(**6**) and (**8**)—(**11**) all gave satisfactory IR, ^1H NMR, ^{13}C NMR, low resolution mass spectral, and microanalytical data.

note that heating a (vinylketene)tricarbonyliron(0) complex has been observed to produce a (η^3-vinylcarbene)tricarbonyliron(0) complex and carbon monoxide,[7] and that coupling of metal-carbenes and isonitriles is a well-established method of generating ketenimines.[5,8] Using this information together with the results of the experiments described above, the pathway outlined in Scheme 3 is proposed for the conversion of (vinylketene)tricarbonyliron(0) complexes into (vinylketenimine)tricarbonyliron(0) complexes.

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