A stereochemical study of the reaction between tricarbonyl(vinylketene)iron(O) complexes and isonitriles

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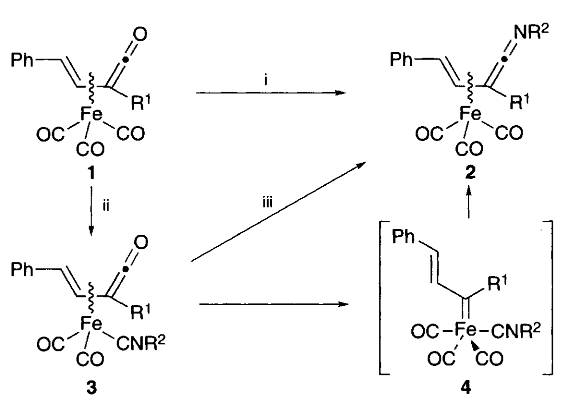
The isonitrile-mediated conversion of tricarbonyl(vinylketene)iron(O) complexes to tricarbonyl(vinylketenimine)iron(O) complexes occurs with retention of configuration at the iron centre revealing that there are no symmetrical species along the reaction coordinate.

Determination of whether a chemical reaction proceeds with retention, racemisation or inversion of configuration at a tetrahedral carbon atom has been used very effectively in organic chemistry to shed light on the mechanistic course of many reactions. In contrast, determination of the stereochemical outcome of organometallic reactions, in which significant modification of organic ligands occurs within the coordination sphere of the metal, has been used relatively sparingly to date in the search for mechanistic information about such processes.[1] In view of this, and in view of current interest in both the synthetic and mechanistic aspects of the chemistry of transition metal complexes of vinylketenes, vinylcarbenes and vinylketenimines,[2] we report herein how a stereochemical study of the isonitrile-mediated conversion of tricarbonyl(vinylketene)iron(O) complexes to tricarbonyl(vinylketenimine)iron(O) complexes led to a refinement of our mechanistic interpretation of this reaction.

Some time ago, we discoverd that heating tricarbonyl(vinylketene)iron(O) complexes **1** in the presence of isonitriles led to the formation of tricarbonyl(vinylketenimine)iron(O) complexes **2**, Scheme 1.[3] Based on the isolation of dicarbonylisonitrile(vinylketene)iron(O) complexes **3** from three of the reaction mixtures and the conversion of each of these compounds into vinylketenimine complexes **2** under the reaction conditions used for the conversion of **1** to **2**, it was established that dicarbonylisonitrile(vinylketene)iron(O) complexes **3** were intermediates in the conversion of **1** to **2**. Furthermore, a careful examination of the product mixture generated when two different dicarbonylisonitrile(vinylketene)iron(O) complexes **3** (R^1 = Me, R^2 = C_6H_{11}; R^1 = R^2 = Bu^t) were heated in the same pot did not detect any evidence for the production of cross-over products, thus suggesting that the carbonyl/isonitrile exchange process that occurs when **3** is transformed into **2** proceeds without dissociation of the isonitrile ligand from the iron centre. Based on (i) this result, (ii) an earlier observation by others that heating a tricarbonyl(vinylketene)iron(O) complex at 60 °C in toluene produces a tricarbonyl(η^3-vinylcarbene)iron(O) complex (a process which is reversed under one atmosphere of carbon monoxide at 20 °C),[4] and (iii) the knowledge that the coupling of metal-carbene and isonitriles is a well-established method of generating ketenimines,[5] we proposed that the η^1-vinylcarbene **4** was an intermediate in the conversion of complexes **1** and **3** to **2**.



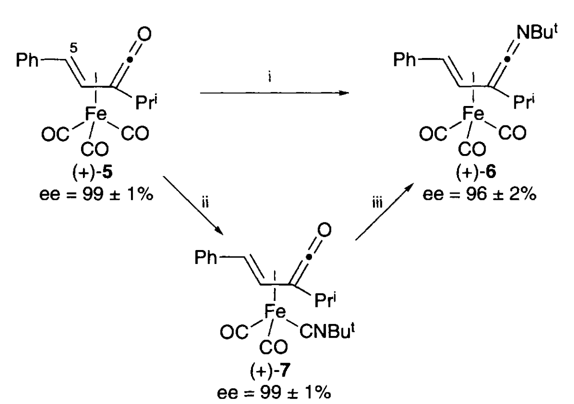
R^1 = Me, Bu^t;

R^2 = Bu^t, cyclohexyl, 2,6-dimethylphenyl, CH(Me)Ph, CH(Me)Bu^t

Scheme 1 *Reagents and conditions*: i, R^2NC, C_7H_8, 80 °C, 10–24 h, 51–71%; ii, R^2NC, C_7H_8, 80 °C, 3–3.5 h, 24–45%; iii, C_7H_8, 80 °C, 10–22 h, 63–68%

We recently devised a route to enantiomerically enriched tricarbonyl(vinylketene)iron(O) complexes and established their absolute configuration.[6] With these compounds in hand, it was decided to determine the stereochemical outcome of the reaction between tricarbonyl(vinylketene)iron(O) complexes and isonitriles. Thus enantiomerically enriched tricarbonyl(3-isopropyl-5-phenyl-1-oxapenta-1,2,4-triene)iron(O) **5** was prepared by reaction of racemic material with 0.5 equiv. of deprotonated (*S*)-α-methylbenzyl diethylphosphoramidate as described previously.[6] The ee of the enriched material was measured by HPLC [Chiralcel OD-H; isopropanol–hexane (1 : 9), 1 cm^3 min^{-1}] and found to be 99 ± 1%, whilst correlation of the optical rotation of the enriched material $\{[\alpha]_D^{25} = +1314 \pm 130$ (*c* 0.75, CH_2Cl_2)$\}$ with that of another sample of **5**, whose absolute configuration had been established previously,[6] revealed that the absolute configuration of the enriched material was 5*pS*.†

Reaction of complex (+)-**5** with *tert*-butylisonitrile (at 40 °C for 1 h, then 50 °C for 1 h and finally 80 °C for 15 h) gave a 65% isolated yield‡ of the tricarbonyl(vinylketenimine)iron(O) complex **6**, Scheme 2.§ The ee of **6** was measured by ^1H NMR spectroscopy [in the presence of (*R*)-(−)-1-(9-anthryl)-2,2,2-trifluoroethanol] and, to our surprise, found to be 96 ± 2%, *i.e.* the conversion of **5** to **6** had occurred without loss of

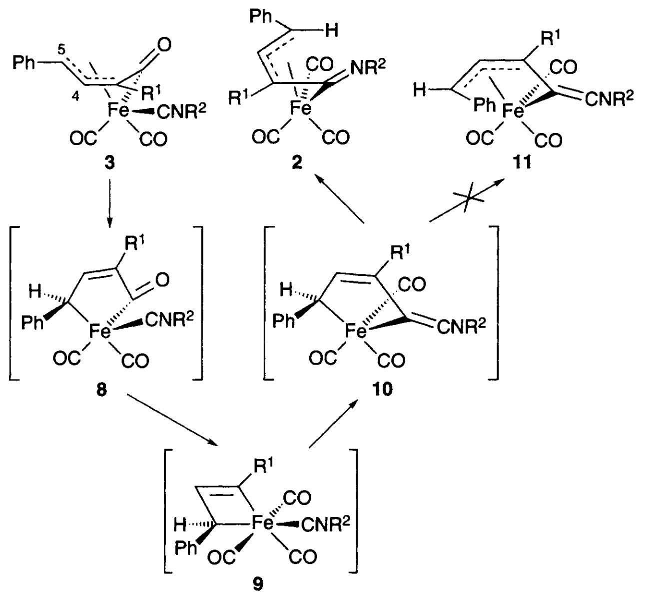


Scheme 2 *Reagents and conditions*: i, Bu^{t}NC, C_7H_8, (*a*) 40 °C, 1 h; (*b*) 50 °C, 1 h; (*c*) 80 °C, 15 h; 65%; ii, Bu^{t}NC, C_7H_8, (*a*) 40 °C, 1 h; (*b*) 50 °C 1 h; (*c*) 80 °C, 1 h; 75%; iii, C_7H_8, 80 °C, 17 h, 90%

stereochemical information and clearly could not proceed *via* any symmetrical intermediates. Comparison of the CD spectrum of **6** with the CD spectra of closely related tricarbonyl(vinylketenimine)iron(0) complexes of known absolute configuration,[8] revealed that the absolute configuration of **6** was 5*pS* and that the conversion of **5** to **6** had occurred with retention of planar chirality.

In order to determine whether the formation of the dicarbonylisonitrile(vinylketene)iron(0) intermediate **7** and its subsequent isomerisation to the tricarbonyl(vinylketenimine)iron(0) complex **6** both proceeded with retention or inversion of planar configuration, the stereochemical consequences of converting the tricarbonyl(vinylketene)iron(0) complex **5** to intermediate **7** and the intermediate **7** to product **6** were probed. Firstly, reaction of **5** with *tert*-butylisonitrile (at 40 °C for 1 h, then 50 °C for 1 h and finally 80 °C for 1 h) gave the substitution product **7** in 75% isolated yield. The ee of **7** was measured and found to be 99 ± 1% by HPLC [Chiralcel OD-H; isopropanol–hexane (1:9), 1 cm^3 min^{-1}] {$[\alpha]_D^{25}$ = +930 ± 90 (*c* 2.1, CH_2Cl_2)}, and its absolute configuration was found to 5*pS* by comparison of its CD spectrum with that of the vinylketene complex **5** and several other closely related tricarbonyl(vinylketene)iron(0) complexes. Secondly, heating intermediate **7** at 80 °C for 17 h gave a 90% isolated yield of **6**. The ee of this second sample of **6** was measured and found to be 96 ± 2% (by ^{1}H NMR spectroscopy); comparison of the optical rotations of the first and second samples of **6** {$[\alpha]_D^{25}$ = +790 ± 80 (*c* 3.4, CH_2Cl_2) and 842 ± 80 (*c* 4.6, CH_2Cl_2)} revealed that the absolute configuration of the second sample of **6** was the same as the first sample. Thus the conversion of the tricarbonyl(vinylketene)iron(0) complex **5** to the dicarbonylisonitrile(vinylketene)iron(0) complex **7** and the conversion of **7** to the tricarbonyl(vinylketenimine)iron(0) complex **6** both proceed with retention of planar configuration.

Clearly the results described above are inconsistent with the proposed intermediacy of the symmetrical intermediate **4** and thus our mechanistic interpretation of the conversion of tricarbonyl(vinylketene)iron(0) complexes to tricarbonyl(vinylketenimine)iron(0) complexes needs to be refined, Scheme 3. Simultaneous coordination of three carbon monoxide and one isonitrile ligands to the iron centre can only be achieved by dissociation of a two electron donor derived from C(3–5) of the organic ligand. Whilst dissociation of C-4 and C-5 and deinsertion of the ketene carbonyl led to the plausible but now discredited symmetrical intermediate **4**, dissociation of C-3 and C-4 and deinsertion of carbon monoxide leads to intermediates **8** and **9** respectively, in which the stereochemical information inherent in the starting material is preserved at C-5. [It is interesting to note that a $(C_5H_5)(PPh_3)Co$ analogue of **9** has been isolated and converted into a vinylketene derivative and a vinylketenimine derivative on treatment with carbon monoxide and *tert*-butylisonitrile respectively.[2d]] Irreversible insertion of the isonitrile ligand into the iron–C(3) bond then gives **10** (isonitrile insertion into metal–carbon bonds is more facile than the corresponding carbonyl insertion, as the iminoacyl group thus formed is thermodynamically more stable than its acyl counterpart),[9] and, finally, re-coordination of the iron to the same face of C-3 and C-4 that it dissociated from generates the observed product **2** (coordination of the iron to the opposite face of C-3 and C-4 would generate the relatively high energy diastereoisomer **11** and is therefore disfavoured).



Scheme 3

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Footnotes

† Application of the Cahn-Ingold-Prelog convention for π-complexes[7] to C-5 of the vinylketene ligand leads to the *S* designation.

‡ Isolation of products was achieved by chromatography; especial care was taken to collect all of the product from the column to avoid chromatographic enantiomer enrichment or depletion.

§ The novel complexes **6** and **7** gave satisfactory spectroscopic (IR, ^{1}H NMR, ^{13}C NMR and low-resolution MS) and microanalytical or high-resolution MS data.

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