

Preliminary communication

Bond shift isomerization in a heterodiene complexed to $\text{Fe}(\text{CO})_3$

Hassan Cherkaoui, Jacques Martelli *, René Grée

Laboratoire de Synthèses et Activations de Biomolécules, CNRS URA 1467, ENSCR, Avenue du Général Leclerc, 35700 Rennes, France

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Abstract

Kinetic studies for the isomerization of a $\text{Fe}(\text{CO})_3$ complexed heterodiene are reported here.

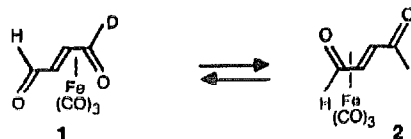
Keywords: Iron; Carbonyl; Kinetic studies; Heterodiene complex

The interconversion of shift isomeric transition metal complexes is a fundamental problem in organometallic chemistry [1]. It has been extensively studied in the case of polyenetetrahaptoiron tricarbonyl complexes. Detailed kinetic experiments have established that the interconversion is rapid in the case of cyclic derivatives, like cyclooctatetraenes or tropones [2]. However, the process is much slower in the case of acyclic polyenes [3]. Furthermore, the electronic effects of substituents on equilibria are small, while their effects on rates of isomerization are somewhat higher [3]. Recent results have quantitatively confirmed these data and furthermore, they have established a strong influence of the iron ligands [4]. These data were clearly of much interest for use in the area of organic synthesis [5], of such acyclic polyenes selectively complexed to $\text{Fe}(\text{CO})_3$: the high activation energies (around 30 kcal mol^{-1}) obtained for the thermal bond–shift isomerization allowed a good regio- and stereocontrol during the reactions occurring on the “free” double bonds. This could be extended later to asymmetric synthesis, since the racemization process is even slower (2.7 times) than the bond-shift.

To the best of our knowledge, there are equivalent data only for the corresponding 1-aza-diene complexes [6]. It is well established that such derivatives are less stable than the corresponding dienes, since they can be used as efficient agents for the transfer of the $\text{Fe}(\text{CO})_3$ unit [7]. However, quantitative data, especially on

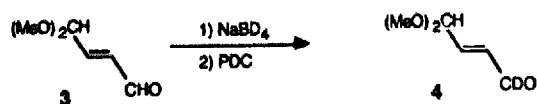
bond–shift isomerization, appear necessary if the use of enone or enals complexed to iron carbonyl moieties in selective organic synthesis is concerned. Due to its easy access and its symmetry, the tricarbonyliron complex of fumaraldehyde [8] is a very attractive model for such a study. Thus, the purpose of this communication is to describe an efficient synthesis of the selectively deuterated complex **1** and to report a detailed kinetic study of its equilibrium with its isomer **2** (Scheme 1).

The synthesis of the monodeuterated fumaraldehyde monodimethylacetal **4** is easily achieved from **3** [9] by reduction with NaBD_4 followed by a PDC oxidation (Scheme 2). This gave an 88:12 ratio (NMR control) of **4** and the non deuterated product **3**. A second, similar sequence gave **4** in 39% overall yield from **3** and with a deuterium content better than 95% (NMR). It is interesting to point out the very high isotopic effect (around 8) observed during this oxidation step. The synthesis of **1** followed the sequence already described for the corresponding non deuterated complex [8]: the reaction of **4** with $\text{Fe}_2(\text{CO})_9$ gave a mixture of **5** and **6** separated by chromatography. The η^2 complex **5** is transformed into **6** by heating in toluene, giving the η^4 complex in 44% overall yield from **4**. The removal of the acetal group using Conia’s method [10] gave **1** in 94% yield, without

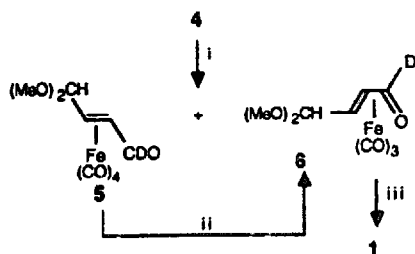


Scheme 1.

* Corresponding author.



Scheme 2.



Scheme 3. (i) $\text{Fe}_2(\text{CO})_9$ (1.2 eq), toluene, 45°C , 135 mm 5 (56%) and 6 (13%); (ii) toluene, 80°C , 180 min 6 (55%); (iii) SiO_2 , 25%, H_2SO_4 , r.t., 50 min, 1 (94%).

bond-shift isomerization (Scheme 3). A deuterium content of $97.8 \pm 0.2\%$ was measured by high resolution mass spectrometry. The isomerization of 1 into 2 was easily followed by ^1H NMR (signals at 9.15 ppm for 1 and 6.83 ppm for 2 in C_6D_6). The reaction, studied at five temperatures between 303 and 323 K, followed clean first order kinetics to give a 1 : 1 mixture of 1 and 2 [11]. An activation energy of $20.9 \pm 0.8 \text{ kcal mol}^{-1}$ was obtained for this process, which is about 10 kcal mol^{-1} lower than the bond-shift isomerization in the corresponding dienyl series [3]. The small negative value ($-10 \pm 2 \text{ e.u.}$) obtained for the entropy of activation indicate a relatively ordered transition state for this process. In conclusion, it is possible to selectively complex an enal system by an $\text{Fe}(\text{CO})_3$ moiety but these new data demonstrate that the bond-shift become more rapid in that case [12]. It will probably limit the use of

such complexes in stereoselective and/or asymmetric synthesis.

References and notes

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- [6] During the preparation of this communication appeared a publication dealing with this problem on a different model: H.-J. Knölker, G. Baum and P. Gonser, *Tetrahedron Lett.*, 36 (1995) 8191.
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- [11] The following values have been obtained: $t = 303 \text{ K}$: $k = 9.92 \cdot 10^{-5} \text{ s}^{-1}$; $t = 308 \text{ K}$: $k = 1.84 \cdot 10^{-4} \text{ s}^{-1}$; $t = 313 \text{ K}$: $k = 2.80 \cdot 10^{-4} \text{ s}^{-1}$; $t = 318 \text{ K}$: $k = 4.80 \cdot 10^{-4} \text{ s}^{-1}$; $t = 323 \text{ K}$: $k = 9.06 \cdot 10^{-4} \text{ s}^{-1}$.
- [12] Preliminary results indicate that substituents effects are small; very close activation energies are also obtained for the isomerization of $\text{Fe}(\text{CO})_3$ complexed unsymmetrical heterodienes (OHC-CH=CH-COR with $\text{R} = \text{Me}$ or Ph , for instance).