Facile α-β isomerisation of the σ-π phenylethenyl ligand at the diiron centre

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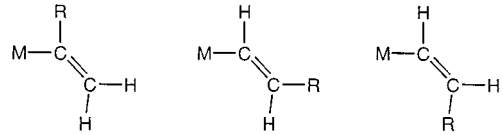
At 110 °C α-substituted $[Fe_2(CO)_6(\mu\text{-}PhC{=}CH_2)(\mu\text{-}PPh_2)]$ 1 is cleanly converted into the β-isomer $[Fe_2(CO)_6(\mu\text{-}HC{=}CHPh)(\mu\text{-}PPh_2)]$ 2, a process which is accelerated in the presence of arylphosphines; with $P(OMe)_3$ mono- and di-substituted adducts of 1 are isolated at 70 °C, which cleanly isomerise at higher temperatures.

The alkenyl ligand has been proposed as a key intermediate for the Fischer–Tropsch process[1] and as a result, the chemistry of this important ligand has been studied at a variety of metal centres, the emphasis of this work being based on carbon–carbon bond forming reactions.[2–4] Monosubstituted alkenyl complexes can adopt isomeric forms **I**–**III** with the substituent

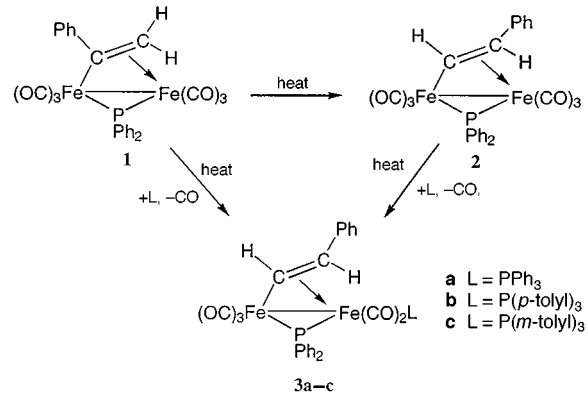


I II III

on either the α- or β-carbon. Interconversion of β-isomers II and III has been noted in a number of instances, and results from rotation about the carbon-carbon bond.[5,6] In contrast, as far as we are aware, and despite the large volume of literature concerning alkenyl complexes, α,β-isomerisation of alkenyl complexes has not been reported. Herein we describe the clean conversion of an α-substituted alkenyl ligand (**I**) to its β-isomer (**II**) at the diiron centre, a process which is accelerated in the presence of arylphosphines.

A convenient route to alkenyl complexes involves the hydrometalation of alkynes, primary alkynes giving both α- and β-substituted isomers depending upon the regioselectivity of the process. Hydrodimetalation of PhC≡CH by $[Fe_2(CO)_7(\mu\text{-}H)(\mu\text{-}PPh_2)]$ is reported to afford a mixture of α-$[Fe_2(CO)_6(\mu\text{-}PhC{=}CH_2)(\mu\text{-}PPh_2)]$ **1** and β-$[Fe_2(CO)_6(\mu\text{-}HC{=}CHPh)(\mu\text{-}PPh_2)]$ **2** substituted isomers in a 4:1 ratio.[7] In our hands, and provided that the temperature is not raised during work-up, the α-isomer **1** is the sole product as shown by ^1H NMR spectroscopy. However, when a toluene solution of **1** was heated at 110 °C for 1 h clean conversion to β-isomer **2** was noted, being isolated in >90% yield after chromatography. Conversion of **1** to **2** is easily followed by ^1H NMR spectroscopy. Under these conditions conversion was quantitative, the appearance of a low-field multiplet being characteristic of the α-proton of an alkenyl ligand. Following the reaction by NMR and IR spectroscopy failed to reveal any intermediates.

In the presence of arylphosphines, alkenyl isomerisation was accelerated. Heating a toluene solution of **1** and PPh_3 to 110 °C for 10 min lead to the quantitative formation of the β-substituted phosphine adduct $[Fe_2(CO)_5(PPh_3)(\mu\text{-}HC{=}CHPh)(\mu\text{-}PPh_2)]$ **3a**.‡ The ^1H NMR spectrum clearly showed that both carbonyl substitution and alkenyl isomerisation had occurred, the α-proton appearing at δ 8.35. Monitoring the reaction by ^{31}P NMR spectroscopy again failed to reveal any intermediates. The acceleration of alkenyl isomerisation was found for other phosphines, including P(*p*-tolyl)$_3$ and P(*m*-tolyl)$_3$ (Scheme 1). In contrast, addition of the more sterically demanding isomer

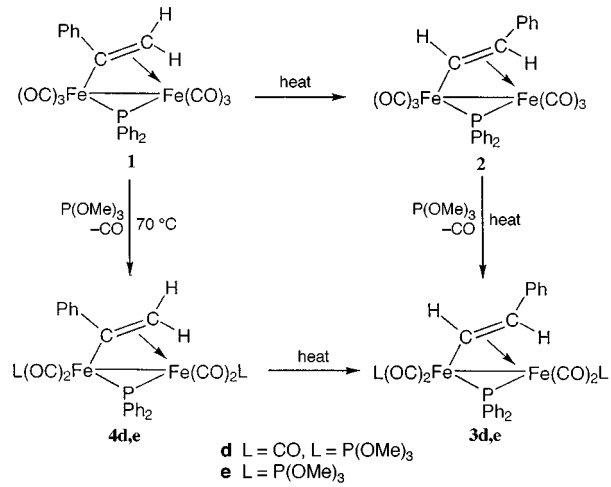


Scheme 1

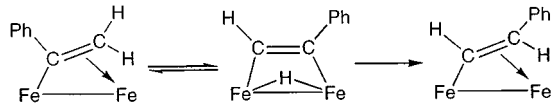
P(*o*-tolyl)$_3$ did not result in accelerated isomerisation, **2** being the sole product, and suggesting that it is carbonyl substitution which accelerates alkenyl isomerisation.

Further insight was gleaned from the reaction of $P(OMe)_3$ with **1** (Scheme 2). This proceeded rapidly (10 min) at 70 °C and led to a mixture of $[Fe_2(CO)_5\{P(OMe)_3\}(\mu\text{-}PhC{=}CH_2)(\mu\text{-}PPh_2)]$ **4d** and $[Fe_2(CO)_4\{P(OMe)_3\}_2(\mu\text{-}PhC{=}CH_2)(\mu\text{-}PPh_2)]$ **4e**.‡ Pertinently, the α-substituted alkenyl ligand is maintained throughout. Warming both **4d** and **e** to reflux in toluene resulted in their rapid (< 10 min) conversion into the β-substituted isomers $[Fe_2(CO)_5\{P(OMe)_3\}(\mu\text{-}HC{=}CHPh)(\mu\text{-}PPh_2)]$ **3d** and $[Fe_2(CO)_4\{P(OMe)_3\}_2(\mu\text{-}HC{=}CHPh)(\mu\text{-}PPh_2)]$ **3e**, respectively, also obtained from the direct reaction of $P(OMe)_3$ with **2**, while reaction of the latter with PPh_3 afforded **3a** in a similar manner.

Conversion of **3** to **4** involves both carbonyl substitution and alkenyl isomerisation. For the arylphosphines utilised to date, carbonyl substitution is rate-determining, being followed by rapid alkenyl isomerisation. In contrast, with the less sterically demanding $P(OMe)_3$, carbonyl substitution is more facile and alkenyl isomerisation becomes rate-determining. While the



Scheme 2



Scheme 3

origin of the rate acceleration of alkenyl isomerisation is not clear, since the β-phenylethenyl ligand is generated in all cases it must be thermodynamically preffered. It is difficult to see how this can be a result of steric effects in the hexacarbonyl complexes and we believe that their must be an electronic preference for the adoption of the β-isomer, while the hydrodimetalation reaction affords the α-isomer preferentially as a result of Markovnikov addition.

The precise manner in which alkenyl isomerisation occurs is as yet unknown. It may simply occur *via* a direct 1,2-proton shift, although it is difficult to see how the rate of such a process would be strongly affected by ligand substitution. A second possibility is that it results from a reversible C–H addition to the diiron centre (Scheme 3). Such a process would afford a hydrido–alkyne intermediate, with the alkyne lying parallel to the diiron vector and acting as a two-electron donor in order to preserve the EAN count of 34. Carbon-hydrogen bond formation from this intermediate would either regenerate the α-isomer or irreversibly afford the thermodynamically favoured β-isomer. Both oxidative addition and reductive elimination are likely to be sensitive to the steric and electronic nature of the other ligands, and this may account for the observed changes in the rate of alkenyl isomerisation.

We are currently investigating whether α–β alkenyl isomerisation is general by studying analogous reactions of other α-substituted complexes $[Fe_2(CO)_6(\mu\text{-}RC{=}CH_2)(\mu\text{-}PPh_2)]$. Further we are trying to gain more mechanistic insight into this transformation *via* reaction of **1** with a wider range of phosphines, phosphites and related reagents, while we are looking for alternative low-temperature routes to phosphine substituted α-alkenyl complexes in order to obtain kinetic information concerning the rate acceleration.

Notes and References

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‡ All compounds exhibit satisfactory spectroscopic and analytical data. *Selected data* for **3a**: ν(CO)(CH_2Cl_2)/cm^{-1} 2034m, 1983vs, 1947s, 1917m, 1884w; δ_H($CDCl_3$) 8.35 (dd, *J* 27.9, 12.9, 6.5, 1H, H_α), 7.9–6.4 (m, 30H, Ph), 4.12 (dd, *J* 12.9, 5.4, 1H, H_β); δ_P($CDCl_3$) 181.2 (d, *J* 93.4, μ-PPh_2), 73.0 (d, *J* 93.4, PPh_3). For **3b**: ν(CO)(CH_2Cl_2)/cm^{-1} 2030m, 1982vs, 1946s, 1917m, 1885w; δ_H($CDCl_3$) 8.35 (ddd, *J* 27.8, 12.9, 6.5, 1H, H_α), 7.8–7.0 (m, 25H, Ph), 6.62 (d, *J* 7.5, 2H, Ph), 4.13 (dd, *J* 12.9, 5.3, 1H, H_β), 2.36 (s, 9H, Me); δ_P($CDCl_3$) 180.6 (d, *J* 93.9, μ-PPh_2), 72.0 (d, *J* 93.9, PPh_3). For **3c**: ν(CO)(CH_2Cl_2)/cm^{-1} 2033m, 1982vs, 1970sh, 1949m, 1915m; δ_H($CDCl_3$) 8.31 (ddd, *J* 27.8, 12.9, 6.5, 1H, H_α), 7.8–7.0 (m, 25H, Ph), 6.58 (d, *J* 7.1, 2H, Ph), 4.08 (dd, *J* 12.8, 5.4, 1H, H_β), 2.37 (s, 9H, Me); δ_P($CDCl_3$) 180.6 (d, *J* 94.4, μ-PPh_2), 70.6 (d, *J* 94.4, PPh_3). For **3d** (two isomers A:B in 2:1 ratio): ν(CO)(CH_2Cl_2)/cm^{-1} 2035s, 1987vs, 1971m, 1958s; δ_H($CDCl_3$) 7.8–7.1 (m, Ph), 3.65 (d, *J* 11.2, Me, 9H, A), 3.60 (d, *J* 11.2, Me, 9H, B), 3.16 (d, *J* 15.2, 1H, B), 3.01 (dt, *J* 15.4, 3.3, 1H, A), 2.28 (dt, *J* 12.1, 3.3, 1H, A), 2.24 (d, *J* 10.5, 1H, B); δ_P($CDCl_3$, 213 K) 188.1 [d, *J* 52.7, P(OMe_3), B], 186.6 [d, *J* 70.2, P(OMe_3), A], 165.0 (d, *J* 70.2, PPh_2, A), 152.5 (d, *J* 52.7, PPh_2, B). For **3e**: ν(CO)(CH_2Cl_2)/cm^{-1} 1997vs, 1962s, 1932m; δ_H($CDCl_3$) 7.8–7.1 (m, 15H, Ph), 3.55 (d, *J* 11.2, 9H, Me), 3.51 (d, *J* 11.2, 9H, Me), 3.00 (d, *J* 16.1, 1H), 2.15 (d, *J* 10.8, 1H); δ_P($CDCl_3$, 213 K) 189.8 [d, *J* 47.0, P($OMe)_3$], 189.1 (d, *J* 71.6), 145.9 (br, PPh_2). For **4d**: ν(CO)(CH_2Cl_2)/cm^{-1} 2037s, 1989vs, 1976s, 1956s, 1928m; δ_H($CDCl_3$, 223K) 8.73 (ddd, *J* 31.8, 12.7, 8.1, 1H, H_α), 7.8–6.8 (m, 15H, Ph), 3.79 (d, *J* 11.1, 9H, Me), 3.73 (t, *J* 14.0, 1H, H_β); δ_P($CDCl_3$, 223 K) 182.6 [d, *J* 154.7, P($OMe)_3$], 177.7 (d, *J* 154.7, PPh_2). For **4e** (two isomers A:B in 6:1 ratio): ν(CO)(CH_2Cl_2)/cm^{-1} 1995s, 1963vs, 1930s, 1910m; δ_H($CDCl_3$, 223 K) 8.74 (ddd, *J* 30.2, 13.0, 8.1, 1H, H_α, A), 8.63 (br, 1H, H_α, B), 7.85–6.8 (m, Ph), 3.96 (br, 1H, H_β, B), 3.79 (d, *J* 11.2, 9H, A), 3.73 (d, *J* 11.2, 9H, Me, B), 3.50 (d, *J* 11.5, 1H, H_β, A), 3.32 (d, *J* 11.0, 9H, A), 3.28 (br, 9H, Me, B); δ_P($CDCl_3$, 223 K) 196.8 [d, *J* 45.5, μ-P($OMe)_3$, B], 188.6 [d, *J* 145.7, P($OMe)_3$, A], 181.0 [d, *J* 150.7, P($OMe)_3$, B], 180.3 [d, *J* 59.8 P($OMe)_3$, A], 165.4 (dd, *J* 145.7, 59.8, PPh_2, A), 159.0 (dd, *J* 150.7, 45.0, PPh_2, B).

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Received in Cambridge, UK, 10th June 1998; 8/04403A