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Alkyl isomerisation in three-coordinate iron(II) complexes†

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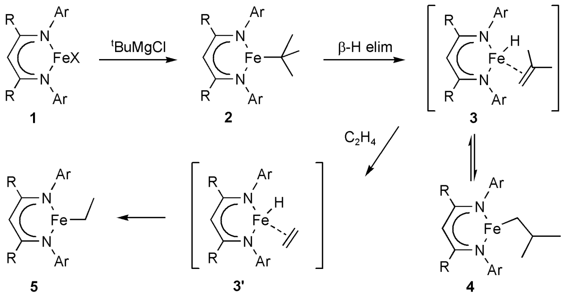
Received (in Purdue, IN, USA) 26th September 2002, Accepted 21st October 2002
First published as an Advance Article on the web 4th November 2002

The *tertiary* to *iso*-butyl isomerisation of three-coordinate iron(II) diketiminate complexes is reported and a hydride intermediate is proposed on the basis of exchange experiments.

Complexes of the late transition metals with bulky bidentate ligands have gained attention because they polymerise ethylene into *highly branched* polyethylene.[1] The mechanisms of propagation, chain transfer, and chain walking in group 10 systems have been studied thoroughly.[2] More recently Gibson, Brookhart, and coworkers have reported iron(II) catalysts that give *linear* polyethylene with high molecular weight.[3] The active catalyst is thought to be a low-coordinate alkyliron(II) complex.[4] The differences in polymer structure suggest that there are differences in the rate of the 'chain walking' process that interconverts linear and branched alkylmetal species. However, the mechanism of isomerisation in low-coordinate alkyliron(II) complexes has not been studied experimentally except by analysis of polymer structure, presumably because of the paramagnetism of the active complexes.[5] A study of relevant diamagnetic cobalt(I) complexes appeared very recently.[6]

This communication describes paramagnetic, low-coordinate butyl complexes of iron(II) and demonstrates that alkyl isomerisation and alkene transfer occur through transient hydride complexes. Bulky β-diketiminate ligands (series **a**: R = *t*Bu; series **b**: R = Me) are used to modify the size of the binding pocket, which is smaller in **1a** than **1b**.[7] Our initial synthetic results are shown along the top and right of Scheme 1. Treatment of iron chloride complex **1a**[7] with *tert*-butylmagnesium chloride in diethyl ether at room temperature yields complex **2a**. When the same reaction is performed with **1b**, only the *iso*-butyl isomer **4b** is isolated. The structures of **2a** and **4b** have been confirmed by X-ray crystallography (Fig. 1)‡ and are similar to the benzyl complex recently reported by Sciarone *et al.*,[8] and to our recently reported alkyl complexes.[9] The products of these reactions are independent of the batch of Grignard reagent or replacement by di-*tert*-butylmagnesium.



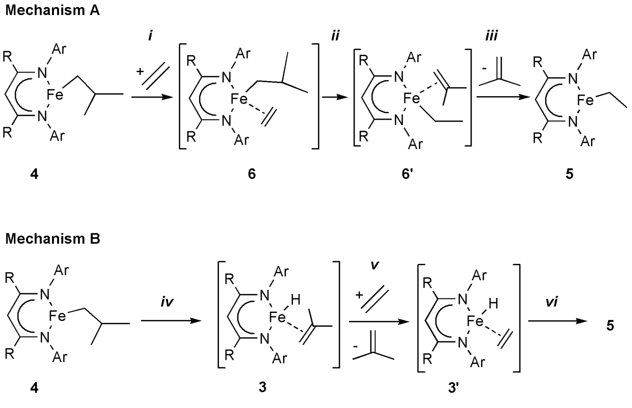
Scheme 1 Preparation and reactions of iron-butyl complexes. Ar = 2,6-diisopropylphenyl. Series **a**: R = *t*Bu, X = Cl. Series **b**: R = Me, X = $Cl_2Li(THF)_2$.

The isomerisation of transition metal alkyl complexes typically leads to more than one isomer at equilibrium.[10] Experiment and theory have shown that electronic factors determine the relative energies of the isomers.[11] Thus linear isomers tend to be favoured for iron and other metals, and *tertiary* alkyl iron complexes are rare.[12]

The formation of the *tert*-butyl compound **2a** with the more sterically demanding ligand leads us to think that **2b** is initially formed during the production of **4b**.§ A plausible mechanism (Scheme 1) to account for *tertiary* to *iso*-butyl isomerisation involves β-hydride elimination to form olefin hydride intermediate **3b**; after rotation or dissociation, reinsertion gives **4b**. The bulkier ligand with R = *tert*-butyl[7] raises the energy of the four-coordinate transition state (relative to **2a**/**2b**) more than the ligand with R = methyl.

In order to establish the existence of **3b**, **4b** was heated at 60 °C in the presence of ethylene. The ^{1}H NMR spectrum showed the clean formation of a new compound, along with isobutylene (Scheme 1). This compound was identified as ethyl complex **5b** by independent synthesis from ethylmagnesium chloride and **1b**, and its structure was determined by X-ray diffraction.‡

The transformation of **4b** to **5b** implicates **3b** as an undetected intermediate. However, another mechanism has been proposed to explain chain transfer in α-olefin polymerisations by late metal catalysts (Scheme 2).[1,5] Mechanism **A** starts with alkene binding (***i***) to form four coordinate alkyl-olefin intermediate **6**, followed by intramolecular hydride transfer (***ii***) and loss of the new alkene (***iii***). Mechanism **B** involves a hydride intermediate **3**, like the one proposed above for butyl isomerisation. We have found that the first-order rate constant for conversion of *iso*-butyl complex **4b** to ethyl complex **5b** is independent of ethylene concentration between 0.1 and 0.9 M. When exchange is monitored with propene or 3,3,3-trifluoropropene instead of ethylene, the rate constants are nearly identical to that for ethylene.¶ These data are inconsistent with mechanism **A**. Moreover, these observations rule out ***v*** and ***vi*** as rate-determining steps, allowing us to conclude that ***iv*** (β-hydride elimination) is rate limiting. An Eyring plot of rate constants in the range 20–74 °C yielded the activation parameters $\Delta H^‡ = +77 \pm 2$ kJ mol^{-1} and $\Delta S^‡ = -70 \pm 8$ J



Scheme 2 Olefin exchange mechanisms.

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† Electronic supplementary information (ESI) available: general considerations, synthesis of compounds, kinetic studies and crystal data. See http://www.rsc.org/suppdata/cc/b2/b209389h/

DOI: 10.1039/b209389h

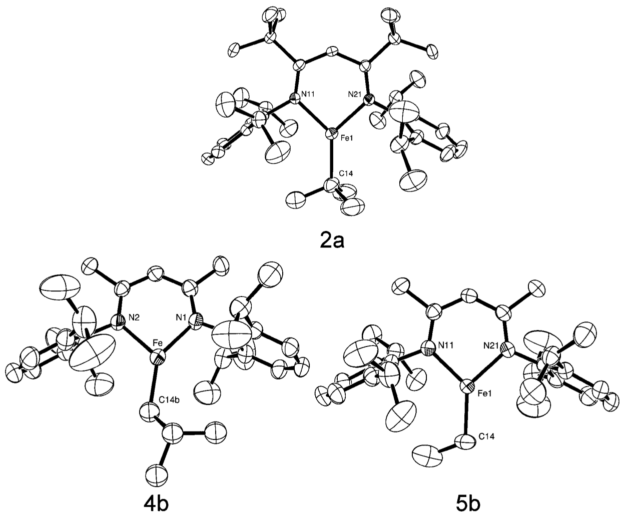

Fig. 1 ORTEP diagrams with thermal ellipsoids at 50% probability. Hydrogen atoms not shown. Selected bond lengths (Å) and angles (°): for **2a**, Fe(1)–N(11) 2.017(2), Fe(1)–C(14) 2.079(4), N(21)–Fe(1)–N(11) 93.10(9), N(21)–Fe(1)–C(14) 133.11(12); for **4b**, Fe–N(1) 1.9830(16), Fe–C(14b) 2.019(6), N(1)–Fe–N(2) 92.77(7), N(2)–Fe–C(14b) 123.43(17); for **5b**, Fe(1)–N(11) 1.9828(19), Fe(1)–C(14) 2.033(3), N(11)–Fe(1)–N(21) 93.44(9), N(11)–Fe(1)–C(14) 132.51(10).

mol^{-1}·K^{-1}. The transition state for ***iv*** is more ordered than **4b**, as expected for β-hydride elimination.

In order to examine directly the isomerisation of an isolated *tert*-butyl complex to an *iso*-butyl complex, we heated *tert*-butyl compound **2a** and found that it converts to **4a** in a first-order process (Scheme 1). The activation parameters of $\Delta H^\ddagger = 85 \pm 5$ kJ mol^{-1} and $\Delta S^\ddagger = -54 \pm 18$ J mol^{-1}·K^{-1} are similar to those for alkene exchange, implying that β-hydride elimination is again rate limiting. The reaction rate is independent of isobutylene concentration, consistent with the mechanism in Scheme 1.

Since **3** lies after the rate-determining step, kinetics do not distinguish whether olefin exchange (***v***) is associative or dissociative. However, heating either a mixture of **4a** and **5b** or a mixture of **4b** and **5a**[9] gave product solutions containing **4a**, **4b**, **5a**, and **5b**. Observation of alkyl crossover suggests that free olefin is formed, assuming that there is no route for direct alkyl exchange between metals. Therefore, it is likely that alkene substitution in **3** follows a dissociative mechanism, and a three-coordinate iron(II) hydride may be transiently formed.

Despite the low coordination number and obvious electronic unsaturation, none of the alkyl complexes reported here have agostic CH···Fe interactions in the solid state. The closest Fe···H contacts in **2a**, **4b** and **5b** are at least 2.50 Å. This contrasts with the bisimine iron complexes reported/modelled by Gibson and Ziegler, for which γ-agostic interactions are proposed to stabilise the active alkyl species.[4,5]

In summary, we have prepared 12-electron iron(II) C$_4$ hydrocarbyl complexes, including a rare example of a *tert*-butyl iron compound that was kinetically trapped using a hindered β-diketiminate ligand. The presence of hydride intermediates explains the kinetics of isomerisation and exchange reactions. The less substituted complexes are favoured thermodynamically, in accordance with predictions based on the polarity of the metal–carbon bond,[11] and this thermodynamic effect is a possible explanation for the linear polyethylene from iron catalysts.

Funding was provided by the National Science Foundation (CHE-0134658) and the University of Rochester. We thank Richard Eisenberg and William Jones for helpful discussions.

Notes and references

‡ *Crystal data* For **2a**, $C_{39}H_{62}FeN_2$, $M = 614.76$, monoclinic, space group $P2_1/n$, $a = 9.7226(5)$, $b = 17.6389(9)$, $c = 21.6557(10)$ Å, $\beta = 96.8150(10)°$, $U = 3687.6(3)$ Å^3, $T = 193(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.436 mm^{-1}, 22 803 reflections measured, 8753 unique ($R_{\text{int}} = 0.0198$), $R_1 = 0.0777$, $wR^2 = 0.1879$, $[I > 2\sigma(I)]$, GOF = 1.128.

For **4b**, $C_{33}H_{50}FeN_2$, $M = 530.60$, monoclinic, space group $P2_1/c$, $a = 20.8440(14)$, $b = 8.6523(6)$, $c = 17.9567(11)$ Å, $\beta = 91.9790(10)°$, $U = 3236.5(4)$ Å^3, $T = 193(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.487 mm^{-1}, 19911 reflections measured, 7792 unique ($R_{int} = 0.0285$), $R_1 = 0.0545$, $wR^2 = 0.1335$, $[I > 2\sigma(I)]$, GOF = 1.041.

For **5b**, $C_{31}H_{46}FeN_2$, $M = 502.55$, monoclinic, space group $P2_1/n$, $a = 15.7646(12)$, $b = 9.3607(7)$, $c = 20.6882(16)$ Å, $\beta = 93.9060(10)°$, $U = 3045.8(4)$ Å^3, $T = 193(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.514 mm^{-1}, 16927 reflections measured, 4823 unique ($R_{int} = 0.0234$), $R_1 = 0.0530$, $wR^2 = 0.1559$, $[I > 2\sigma(I)]$, GOF = 1.025.

2a: Yield 71%; Analysis found(calcd.) C, 76.40(76.19)%, H, 10.03(10.17)%, N, 4.45(4.56)%; μ_{eff}(Evans) = 5.6(3) μ_B; ^{1}H NMR (δ/ppm, 400 MHz, C_6D_6, 21 °C): 130 (br s, 1H, β-CH), 128 (br s, 9H, ^{t}Bu-CH$_3$), 44 (br s, 18H, C(CH$_3$)$_3$), −5 (s, 4H, *m*-CH), −29 (s, 12H, ^{i}Pr-CH$_3$), −110 (s, 2H, *p*-CH), −116 (br s, 12H, ^{i}Pr-CH$_3$), −143 (br s, 4H, ^{i}Pr-CH); Vis (pentane): 510 nm (510 M^{-1}cm^{-1}).

4b: Yield 86%; Analysis found(calcd.) C, 74.10(74.70)%, H, 9.56(9.50)%, N, 5.24(5.28)%; μ_{eff}(Evans) = 6.0(3) μ_B; ^{1}H NMR (δ/ppm, 400 MHz, C_6D_6, 21 °C): 130 (br s, 1H, β-CH), 106 (br s, 6H, ^{i}Bu-CH$_3$), 70 (br s, 6H, α-CH$_3$), −12 (s, 4H, *m*-CH), −18 (s, 12H, ^{i}Pr-CH$_3$), −74 (s, 2H, *p*-CH), −115 (br s, 12H, ^{i}Pr-CH$_3$), −132 (br s, 4H, ^{i}Pr-CH); Vis (pentane): 463 nm (810 M^{-1}cm^{-1}), 490 nm (720 M^{-1}cm^{-1}).

5b: Yield 85%; Analysis found(calcd.) C, 73.29(74.09)%, H, 8.78(9.23)%, N, 5.45(5.57)%; μ_{eff}(Evans) = 5.6(3) μ_B; ^{1}H NMR (δ/ppm, 400 MHz, C_6D_6, 21 °C): 130 (br s, 1H, β-CH), 69 (br s, 6H, α-CH$_3$), −12 (s, 4H, *m*-CH), −20 (s, 12H, ^{i}Pr-CH$_3$), −76 (s, 2H, *p*-CH), −123 (br, 16H, ^{i}Pr-CH$_3$, ^{i}Pr-CH); Vis (pentane): 461 nm (740 M^{-1}cm^{-1}), 489 nm (750 M^{-1}cm^{-1}).

CCDC 194485–194487. See http://www.rsc.org/suppdata/cc/b2/b209389h/ for crystallographic files in CIF or other electronic format.

§ A transient intermediate can be observed by ^{1}H NMR spectroscopy upon mixing of **1b** and Grignard reagent, but attempts to isolate this species or unambiguously characterise it by low temperature NMR and electronic absorption spectroscopies were unsuccessful.

¶ Rate constants at 63 °C (k_{obs}/s^{-1}): ethylene $1.82(9) \times 10^{-3}$; propene $2.2(1) \times 10^{-3}$; 3,3,3-trifluoropropene $1.56(6) \times 10^{-3}$. These data are also consistent with rate-determining alkene dissociation, but the negative value of $\Delta S^\ddagger$ argues against this possibility.

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