Supplementary information for:

Alkyl isomerisation in three-coordinate iron(II) complexes

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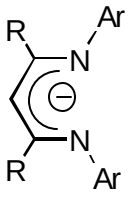
General considerations

Manipulations were performed under a nitrogen atmosphere by standard Schlenk techniques or in an M. Braun Unilab N_2-filled glove box maintained at or below 1 ppm of O_2 and H_2O. Glassware was dried at 150 °C overnight. Proton NMR data were recorded on a Bruker Avance 400 spectrometer (400 MHz) at the specified temperature. Shifts are reported in ppm, relative to residual protiated solvent in C_6D_6 (δ 7.15). Solution magnetic susceptibilities were determined by Evans' method.[13] Microanalysis was performed by Desert Analytics (Tucson, AZ). Pentane, diethyl ether, tetrahydrofuran (THF), and toluene were purified by passage through activated alumina and "deoxygenizer" columns from Glass Contour Co. (Laguna Beach, CA). Deuterated benzene was dried over CaH_2, then over Na, and then vacuum distilled into a storage container or directly into the NMR tube. Ethylene (99.5+%), propylene (99+%) and 3,3,3-trifluoropropene (99%) were used as purchased from Aldrich, 2-methylpropene (isobutylene, 99%) was further purified by vacuum transfer into a Schlenk bomb containing activated molecular sieves and stored overnight prior to use. Precursors L'Li[14], $FeCl_2(THF)_{1.5}$[15] and LFeCl (**1a**)[9] were prepared as described previously. Compound LFeEt (**5a**) is described in reference 9. Ethylmagnesium chloride (2 M in THF) and *tert*-butylmagnesium chloride (2 M in diethyl ether) were purchased from Aldrich and used as received.



Diketiminate ligands used in this work
L : R = *t*-Bu ; Ar = 2,6-di-*iso*-propylphenyl
L' : R = Me ; Ar = 2,6-di-*iso*-propylphenyl

1. Synthesis of compounds

L'FeCl$_2$Li(THF)$_2$ (1b). This compound and its properties have been reported previously by our group.[7] To a slurry of $FeCl_2(THF)_{1.5}$ (2.96 g, 12.8 mmol) in THF (4 mL) was added a solution of, L'Li (5.39 g, 12.7 mmol) in THF (4 mL). After stirring at room temperature for 24 hours, the solution was filtered, concentrated and cooled to -30°C to give yellow crystals of **1b** (7.91 g, 90.7%). Analysis found(calcd.) C, 63.88(63.89)%, H, 8.37(8.25)%, N, 4.11(4.02)%; μ_{eff}(Evans) = 5.4(3) μ_B; ^{1}H NMR (δ/ppm, 400 MHz, THF-d_8, 21°C): 15 (s, 6H, α-CH_3), 7 (br s, 1H, β-CH), -17 (br s, 12H, ^{i}Pr-CH_3), -33 (br s, 4H, ^{i}Pr-CH), -44 (s, 2H, *p*-CH), -65 (br s, 12H, ^{i}Pr-CH_3).

LFe(*tert*-C$_4$H$_9$) (2a). A solution of *tert*-butylmagnesium chloride (820 µL, 1.63 mmol) was added to a solution of **1a** (1.00 g, 1.63 mmol) in diethyl ether. After stirring for 2 h at room temperature, the solution was filtered through Celite, concentrated and cooled to -30°C to give red crystals of **2a** (715 mg, 71.4%). 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, α-$C(CH_3)_3$), -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 $M^{-1}cm^{-1}$).

L'Fe(*iso*-C$_4$H$_9$) (4b). *tert*-Butylmagnesium chloride (870 µL, 1.44 mmol) was added to a solution of **1b** (1.00 g, 1.44 mmol) in toluene. After stirring for 2 h at room temperature, the solution was filtered through Celite and the solvent pumped down. The yellow solid was redissolved in 2 mL pentane and recrystallysed at -30°C (658 mg, 86.1%). 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 $M^{-1}cm^{-1}$).

L'Fe(C_2H_5) (5b). A solution of ethylmagnesium chloride (144 µL, 288 µmol) was added to a solution of **2b** (200 mg, 288 µmol) in toluene. After stirring for 2 h at room temperature, the solution was filtered through Celite and the solvent pumped down. The light yellow solid was redissolved in 1 mL pentane and recrystallysed at -30°C (144 mg, 85.0%). 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 $M^{-1}cm^{-1}$).

2. Kinetic studies

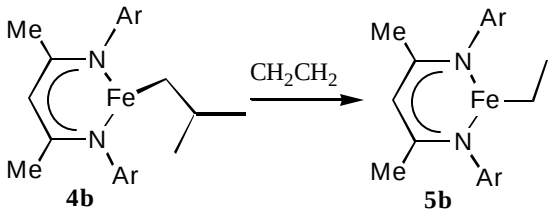
2.a Olefin exchange

A known amount of gaseous olefin was condensed from a calibrated volume bulb into a J. Young NMR tube immersed in a liquid nitrogen bath containing a solution of **4b** (*ca.* 45 mM) in C_6D_6. The tube was then placed in the NMR spectrometer probe at the given temperature (calibrated using the ethylene glycol method[16]). Spectra were collected periodically. A solution of complex **1a** in C_6D_6 in a sealed capillary tube was used as an internal standard.[17] No significant variation on the total iron concentration *vs*. internal standard was observed over time and no intermediates were observed by NMR. After completion, isobutylene could be identified in the volatile materials extracted from the reaction mixture by ^{1}H NMR (δ in ppm/C_6D_6: 1.87 s, 2H; 1.59 s, 6H) and GC-MS (*m*/*z* : 56).

After Fourier transform, phasing, calibrating and integrating each spectrum, a plot of normalized **4b** concentration (y) *vs.* time (M0) was used to find the best fit to the general, integrated kinetic equation:

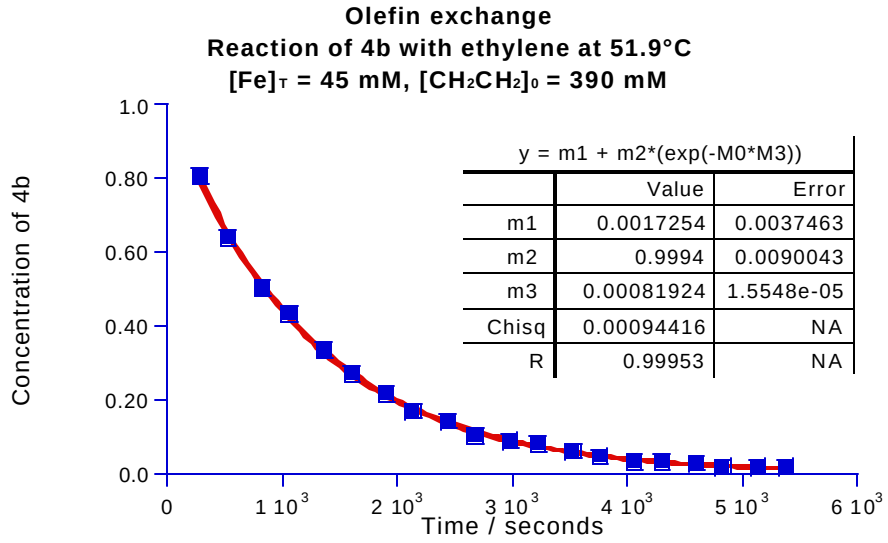
$$y = m1 + m2*(\exp(-M0*M3))$$

where m1, m2 and M3 are variables, M3 being the first order rate constant. For this purpose, KaleidaGraph 3.51 was used. A representative curve and the final Eyring plot for the ethylene exchange experiments are shown below.



4b **5b**

Ar = 2,6-di-*iso*-propylphenyl



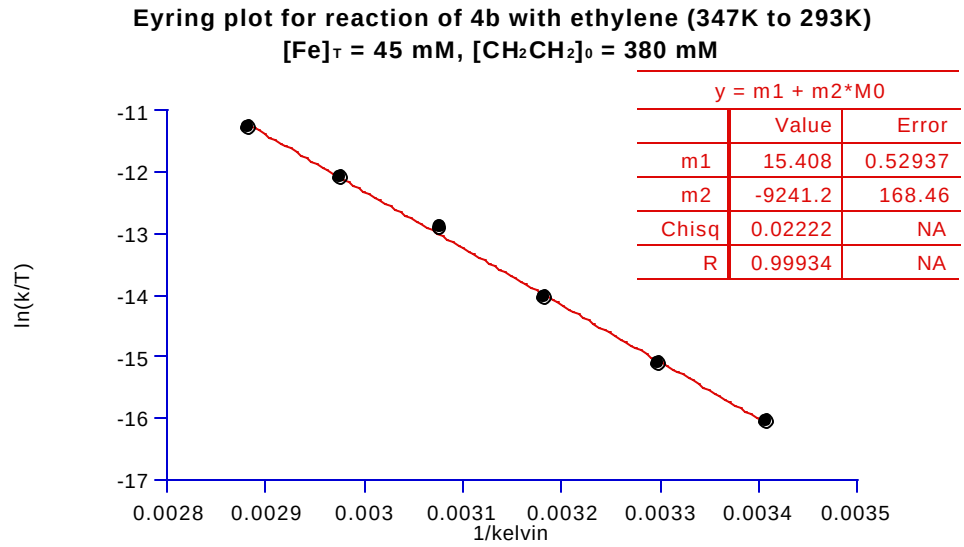
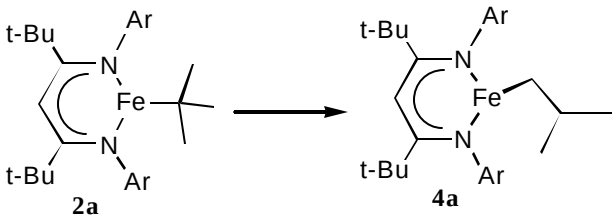


Table 1. Eyring plot data for the reaction of 4b with ethylene.

T / K	k / s^{-1}
346.9(2)	$4.5(1) \times 10^{-3}$
336.0(2)	$1.89(1) \times 10^{-3}$
325.0(2)	$8.2(1) \times 10^{-4}$
314.1(2)	$2.48(4) \times 10^{-4}$
303.2(2)	$8.3(1) \times 10^{-5}$
293.4(2)	$3.1(7) \times 10^{-5}$

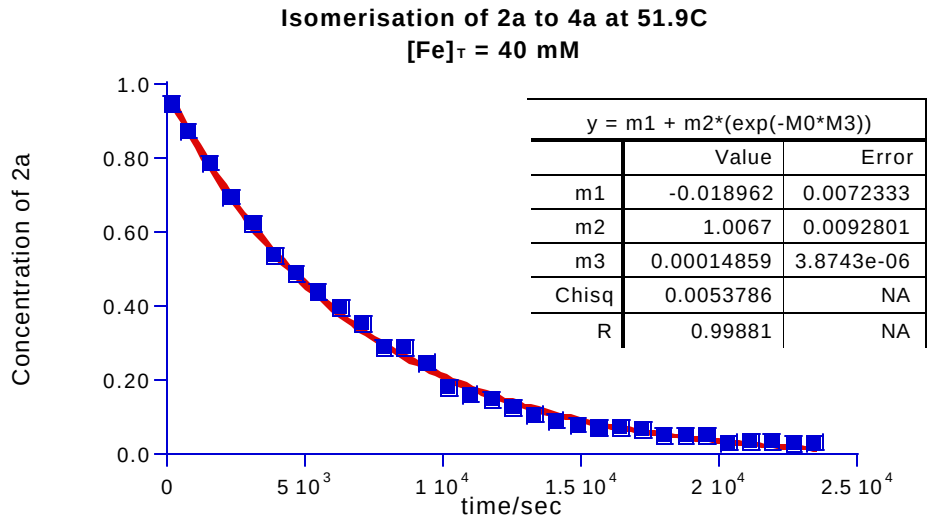
2.b Isomerisation of butyl complex 2a.

Kinetic data were recorded by a similar procedure to olefin exchange experiments starting from pure samples of **2a** (*ca.* 40 mM) in C_6D_6. A sample plot and final Eyring fit are shown below.



2a **4a**

Ar = 2,6-di-*iso*-propylphenyl



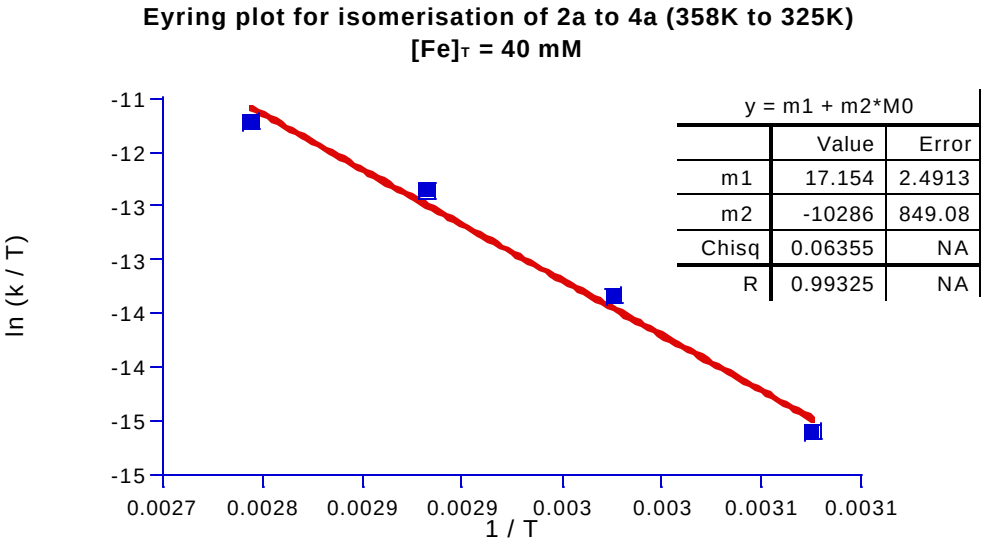
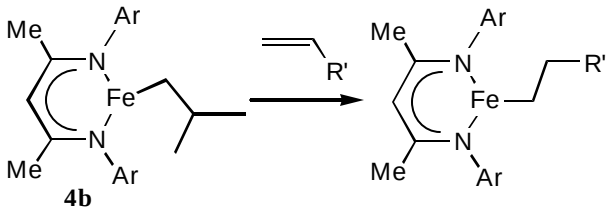


Table 2. Eyring plot data for isomerisation of 2a to 4a.

T / K	k / s^{-1}
357.8(2)	$2.9(3) \times 10^{-3}$
346.9(2)	$1.50(4) \times 10^{-3}$
336.0(2)	$5.4(1) \times 10^{-4}$
325.0(2)	$1.49(3) \times 10^{-4}$

2.c Dependence of rates on olefin concentration. The procedure above was followed after varying the total volume of olefin into the reaction tube. No olefin dependence was obtained as shown below.



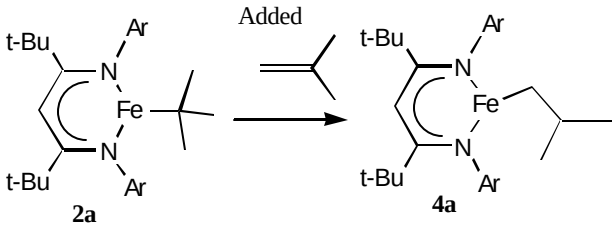
4b

Ar = 2,6-di-*iso*-propylphenyl

Table 3. Olefin exchange data at 336.0K*

R	$[Fe]_T$ / mM	$[olefin]_0$ / mM	k / s^{-1}
H	41	380	0.0018(9)
H	45	128	0.00186(2)
H	110	840	0.00183(9)
H	45	760	0.00182(9)
Me	49	211	0.0021(1)
Me	49	485	0.0023(1)
Me	49	823	0.0021(1)
CF_3	49	319	0.00161(5)
CF_3	49	490	0.00150(6)

*Solvent: C_6D_6.



2a **4a**

Ar = 2,6-di-*iso*-propylphenyl

Table 4. Isomerisation of 2a to 4a at 346.9K*

$[Fe]_T$ / mM	$[isobutylene]_0$ / mM	k / s^{-1}
40	0	0.00049(5)
40	140	0.00043(8)
40	328	0.00047(2)

*Solvent: C_6D_6.

3. Crystal data

X-ray Structural Determination of $C_{39}H_{62}FeN_2$ (2a), $C_{33}H_{50}FeN_2$ (4b), and $C_{31}H_{46}FeN_2$ (5b). Crystalline samples of the three complexes were grown in the glove box from pentane solutions at -30°C . All samples were rapidly mount ed under Paratone-8277 onto glass fibers, and immediately placed in a cold nitrogen stream at -80 °C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Bruker-axs SMART CCD Area Detector System equipped with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1321 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of 30 sec/frame for **2a**, 10 sec/Frame for **4b**, and 60 sec/Frame for **5b** using a detector-to-crystal distance of 5.09 cm. The total data collection time was approximately 7, 13, and 26 hours for 10, 30, and 60 sec data respectively. Frames were integrated to a maximum 2θ angle of 56.5° with the Bruker-axs SAINT program. Laue symmetry revealed monoclinic crystal systems for all three crystals. The final unit cell parameters (at -80 °C) were determined from the least-squares refinement of three dimensional centroids of >4000 reflections for each crystal. Dat a were corrected for absorption with the SADABS[18] program.

The space groups were assigned as $P2_1/n$ (#14) for **2a** and **5b**, and $P2_1/c$ (#14) for **4b**, and the structures were solved by direct methods using Sir92[19] (WinGX v1.63.02) and refined employing full-matrix least-squares on F^2 (Bruker-axs, SHELXTL-NT[20], version 5.10). Z values were as expected for one full molecule in the asymmetric unit of each. All non-H atoms in all three complexes were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions. The structures refined to goodness of fit (GOF)[21] values and final residuals[22] found in footnotes.

Notes and references

13 E.M. Schubert, *J. Chem. Ed.*, 1992, **69**, 62; D.F. Evans, *J. Chem. Soc.*, 1959, 2003.

14 M. Chi ng, D.R. Moore, J.J. Reczek, B.M. Chamberlain, E.B. Lobkovsky and G.W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 8738; J. Feldman, S.J. McLain, A. Parthasarathy, W.J. Marshall, J.C. Calabrese and S.D. Arthur, *Organometallics*, 1997, **16**, 1514; A new ligand synthesis has been reported by Power's group: M. Stender, R.J. Wright, B.E. Eichler, J. Prust, M.M. Olmstead, H.W. Roesky and P.P. Power, *J. Chem. Soc., Dalton Trans.*, 2001, 3465.

15 R.J. Kern, *J. Inorg. Nucl. Chem.*, 1962, **24**, 1105.

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17 Chloride complex **1a** was used as an internal standard because is a paramagnetic iron(II) complex with similar NMR parameters (*e.g.* relaxation times, peak broadness) to the compounds studied.

18 The SADABS program is based on the method of Blessing; see Blessing, R.H. *Acta Crystallogr., Sect A* 1995, **51**, 33.

19 A. Altomare, G. Cascarano, C. Giacovazzo and A. Gualardi, *J. Appl. Cryst.*, 1993, **26**, 343.

20 *SHELXTL NT: Structure Analysis Program, version 5.10*; BRUKER-axs: Madison, WI, 1995.

21 $GOF = \left[\sum\left[w\left(F_o^2 - F_c^2\right)^2\right] / \left(n - p\right)\right]^{1/2}$, where n and p denote the number of data and parameters

22 $R_1 = \left(\sum\left||F_o| - |F_c|\right|\right) / \sum|F_o|$; $wR_2 = \left[\sum\left[w\left(F_o^2 - F_c^2\right)^2\right] / \sum\left[w\left(F_o^2\right)^2\right]\right]^{1/2}$

where $w = 1/\left[s^2\left(F_o^2\right) + (a \cdot P)^2 + b \cdot P\right]$ and $P = \left[\left(Max; 0, F_o^2\right) + 2 \cdot F_c^2\right] / 3$