Photoisomerisation of the Diiron Carbonyl Species on the Acenaphthylene Ligand: the First Photo-directed 'Switching' of the Coordination Site of Bimetallic Species on Aromatic Hydrocarbons

Hideo Nagashima,* Takahiko Fukahori and Kenji Itoh

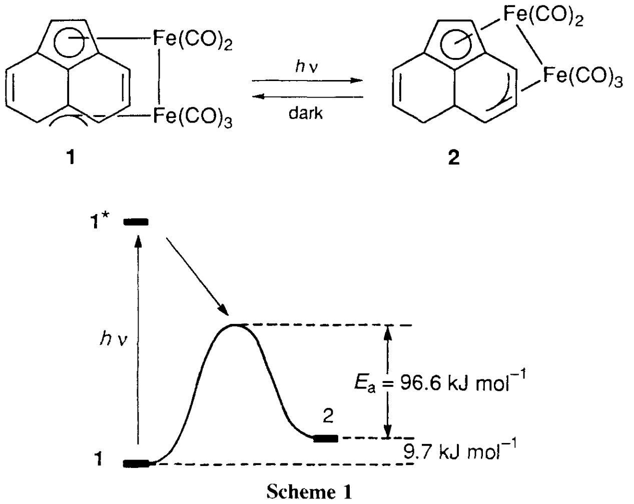
Department of Materials Science, Toyohashi University of Technology, Toyohashi, Aichi 441, Japan

Irradiation of (μ_2-η^3 : η^5-acenaphthylene)$Fe_2(CO)_5$ **1** gave a novel metastable haptotropic isomer **2** (X-ray structure supported), which regenerated **1** in solution upon keeping in the dark.

Among the experimental and theoretical studies for the haptotropic rearrangement,[1] only a few have investigated the reversible exchange of coordination sites of bimetallic species,[2–6] which could provide a substantial change in the physical properties on metal complexes by the reallocation of the metal–metal array on delocalized π-electrons. In this sense, the selective formation and interconversion of haptotropic isomers are of great importance to achieve this 'switching' property of the metal.

We report here the first controllable haptotropic rearrangement between the two isolable bimetallic complexes, in which the direction of the isomerisation can be determined by either irradiation or protection from the light. As shown in Scheme 1, photoisomerisation of a symmetrical isomer of (μ_2-η^3 : η^5-acenaphthylene)$Fe_2(CO)_5$ **1**[7,8] produces a novel unsymmetrical haptotropic isomer **2**, which undergoes thermal reverse isomerisation in the dark to regenerate **1**.

The symmetrical isomer **1** was first prepared by King,[7] and the structure determination was carried out by Churchill.[8] Irradiation of a [$^2H_6$]benzene solution of **1** at room temperature with a 400 W high pressure Hg lamp for 1 h or in sunlight for 2 h results in the conversion of **1** to **2** (>98%) from the ^1H NMR spectrum. Experiments using UV cut-off filters revealed that the visible light (520 nm $< \lambda <$ 690 nm) successfully induced the isomerisation. The acenaphthylene ligand in ^1H and ^{13}C NMR spectra of **2** showed eight proton peaks and twelve carbon peaks, respectively, consistent with the unsymmetrical structure.† Three sharp signals in a 1 : 3 : 1 ratio appeared in the terminal carbonyl region of the ^{13}C NMR spectrum from 0 °C to −80 °C in [$^2H_8$]toluene, indicating the rapid scrambling of three CO ligands on the $Fe(CO)_3$ moiety in solution. However, the IR spectrum (KBr) showed an absorption at 1856 cm^{-1} indicative of the presence of a bridging interaction of the CO ligand in the solid state.†



Scheme 1

An X-ray structure determination was carried out on a single crystal of **2** obtained by cooling the irradiated solution of **1** in a mixture of hexane and ether.‡ The ORTEP drawing of **2** is shown in Fig. 1. The isomerisation resulted in the shift of the $Fe(CO)_3$-moiety to the unsymmetrical η^3-coordination site. The acenaphthylene ligand is slightly distorted. One of the CO groups in the $Fe(CO)_3$-moiety in **2** showed a semi-bridging interaction with the $Fe(CO)_2$-moiety, which is consistent with the IR data described above. The potential formation of the isomer **2** has already been discussed by Churchill,[8] who pointed out that the configuration of **2** would be unfavourable to keep the appropriate iron–iron bond length (2.769 Å in **1**) and planar structure of the acenaphthylene ligand. In the actual structure of **2**, the relatively longer iron–iron bond distance (2.802 Å) produces a weaker metal–metal interaction, which is compensated by the semi-bridging interaction of the CO ligand to the metal centre.

The isomer **2** is not stable in solution protected from the light and slowly regenerates the original complex **1**. This reverse isomerisation showed a first-order dependence on the concentration of **1** with rate constants ($k \times 10^5/s^{-1}$; measured by ^1H NMR in [$^2H_8$]toluene) of 1.70 ± 0.1, 4.26 ± 0.03, and 11.0 ± 0.7 at 288, 295 and 303 K, respectively [E_a = 96.6 kJ mol^{-1}; $\Delta H^\ddagger$ and $\Delta S^\ddagger$ at 298 K, 89.9 kJ mol^{-1} and −25.6 J (mol K^{-1})]. The thermal equilibrium constants, [**2**]/[**1**], estimated from ^1H NMR spectra in the dark, were 0.021, 0.027, 0.035 at 296, 313 and 353 K, respectively, indicating that the isomer **1** is thermodynamically more stable than the isomer **2** by 9.7 kJ mol^{-1}. Thus, the energy profile of the present reversible isomerisation can be illustrated as in Scheme 1. The result that photoexcitation realizes the isomerization to the thermodynamically unfavoured isomer is similar to the well-known photo-induced *cis/trans* isomerisation of alkenes.

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† *Spectral data* for **2**; ^1H NMR ([$^2H_8$] toluene) δ 2.48 (d, *J* 6.35 Hz), 3.28 (d, *J* 2.44 Hz), 4.30 (d, *J* 2.44 Hz), 4.95 (d, *J* 6.35 Hz), 5.26 (d, *J* 6.35 Hz), 5.48 (d, *J* 6.84 Hz), 6.08 (d, *J* 8.79 Hz), 6.14 (dd, *J* 6.84 and 8.79 Hz). ^{13}C NMR ([$^2H_2$]toluene at −60 °C) acenaphthylene region; δ 57.53, 58.26, 71.56, 71.62, 79.64, 83.59, 87.28, 103.73, 114.07, 118.46, 131.78, 146.14, carbonyl region; 215.83, 216.68, 220.87 (peak intensity = 1 : 3 : 1). IR/cm^{-1} (KBr) 2027, 1982, 1961, 1935, 1856.

‡ *Crystal data* for **2**: $C_{17}H_8O_5Fe_2$, black crystal, space group $P\bar{1}$, triclinic, *a* = 8.915(5), *b* = 12.923(7), *c* = 8.032(5) Å, α = 91.29(6), β = 124.74(4), γ = 98.19(5)°, *Z* = 2. Data were measured on a Rigaku AFC-5 automated four-circle diffractometer with Mo-Kα radiation (λ = 0.71068 Å) from a graphite monochromator, and refined by least-squares fit of 20 independent reflections with 25° $< 2\theta <$ 30°. Intensity data were measured by the ω-2θ scan technique (scan range; 2° $< 2\theta <$ 55°, scan speed 8° min^{-1}). All data processing was performed on a FACOM A-70 computer by using the R-CRYSTAN structure solving program obtained from the Rigaku Corp. Neutral scattering factors were obtained from International Tables for X-ray Crystallography (vol. IV); Kynoch Press: Birmingham, UK (1974). In reducing data Lorentz and polarization corrections were made and no absorption correction was made (μ = 18.729 cm^{-1}). The position of the Fe atoms were revealed by the inspection of a Patterson map. Subsequent difference Fourier maps revealed the positions of all other atoms. All hydrogen atoms were located from a difference Fourier map. Final cycle of full-matrix least-squares refinement for the non-hydrogen atoms and isotropic hydrogen atoms converged at *R* = 0.0412 and R_w = 0.0365 of 3324 unique data [$F > 3\sigma(F)$] from 3687 total collection data. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

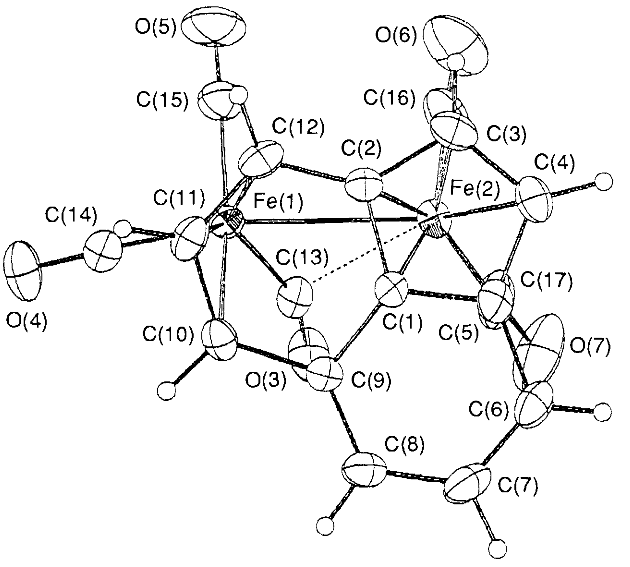

Fig. 1 ORTEP drawing of **2**. Selected bond distances (Å) and angles (°): Fe(1)–Fe(2) 2.802 (1), Fe(1)–C(10) 2.194 (3), Fe(1)–C(11) 2.056 (4), Fe(1)–C(12) 2.160 (3), Fe(2)–C(1) 2.112 (3), Fe(2)–C(2) 2.110 (4), Fe(2)–C(3) 2.104 (4), Fe(2)–C(4) 2.099 (3), Fe(2)–C(5) 2.180 (3), Fe(1)–C(13) 1.799 (5), Fe(2)–C(13) 2.487 (2); Fe(1)–C(13)–O(3) 159.32 (25).

It is known that photo-irradiation of dinuclear metal carbonyl complexes usually results in either dissociation of the coordinated CO ligands or homolysis of the metal–metal bond.[9] Although the mechanism of the present photo-induced haptotropic rearrangement requires further study, the outcome of the irradiation of **1** suggests that photochemistry can influence the haptotropic rearrangement to produce the thermodynamically unfavoured isomer. We are currently concentrating detailed studies on the mechanism of this photoisomerisation and other photo-induced haptotropic rearrangements of dinuclear metal complexes.

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