# A Reinvestigation of the Solution Structure and Dynamics of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$, $n = 1$ or 2†

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The $^1H$ and $^{13}C$ NMR spectra of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$, $n = 1$ or 2, have been reinvestigated. It is shown that $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(CNMe)]$ exists in $CD_2Cl_2$ as all four possible interconverting isomers, and the activation energy for (μ-CO)(μ-CNMe) bridge opening and closing has been determined as 9.4 kcal $mol^{-1}$. This is believed to be the first determination of the activation energy for the opening of a μ-CNMe, where no other dynamic process is required to occur to obtain the product. The compound $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ exists in $CD_2Cl_2$ solution as only two of the six possible isomers, which are identified as *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$ and *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$.

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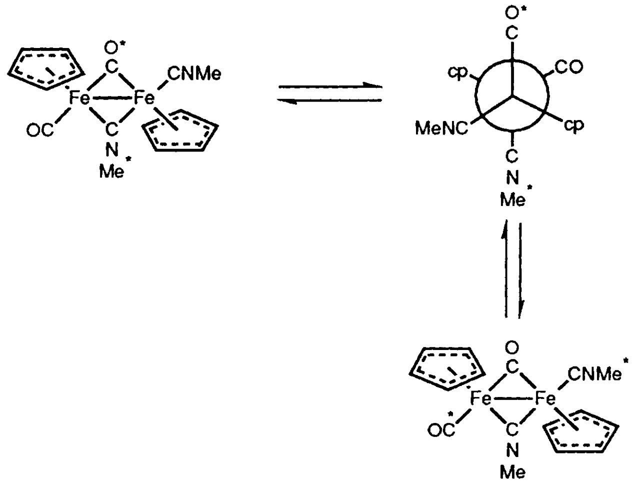
The structures of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$, $n = 1$–3, have been previously investigated by IR and NMR spectroscopy,[1] and the X-ray structure[2] of *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$ has been reported. For $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(CNMe)]$ in $CS_2$–$CD_3C_6D_5$ (3:1) it was concluded that this compound exists in solution as a mixture of either *cis*- or *trans*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_2(CO)(CNMe)]$ (major isomer) and *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2(\mu\text{-}CNMe)]$.[1a] The two isomers exchange with $E_a = 14.0 \pm 1$ kcal $mol^{-1}$, $\log A = 12.5 \pm 1.0$. Subsequent IR spectroscopic investigations of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(CNR)]$ showed that all four isomers are present,[2] but due to the limitations of IR spectroscopy no firm conclusions could be drawn about their relative concentrations or dynamics. The fluxionality of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(CNBu^t)_2]$ has been examined.[3] X-Ray structure determinations have been performed on *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_2(CO)(CNBu^t)]$,[4] *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2(\mu\text{-}CNPh)]$,[5] and *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_2(CO)(CNBu^s)]$.[6] The $^{13}C$ NMR spectra of *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_2(CO)(CNBu^t)]$ and *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2(\mu\text{-}CNPh)]$ have also been reported.[7]

For $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ in $C_6H_4Cl_2$-1,2 it was concluded that this compound exists in solution as a mixture of *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$ and *trans*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$. A crystal structure showed the presence in the solid state of *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$.[2] Two dynamic processes were identified. At 45 °C, the interconversion of the inequivalent cyclopentadienyl and methyl signals of the isomer believed to be *trans*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$ occurs with $\Delta G^\ddagger = 17.5$ kcal $mol^{-1}$. This was believed to be due to opening the (μ-CO)(μ-CNMe) bridge and closing the bridge using the terminal (CO)(CNMe) pair of ligands, see Scheme 1.



**Scheme 1** The mechanism proposed by Adams and Cotton[1b] to account for cyclopentadienyl and methyl exchange in *trans*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$ above room temperature. cp = $\eta^5\text{-}C_5H_5$

A higher-energy process interconverts *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$ and *trans*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$, presumably with Fe–Fe bond rotation with $\Delta G^\ddagger = 18.9$ kcal $mol^{-1}$, see Scheme 2.

A subsequent study[1c] showed that for $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ in $CS_2$ a low-energy dynamic process occurs, which arises from the bend in the C–N–$CH_3$ bond of the μ-CNMe groups, with $\Delta G^\ddagger = 11.0 \pm 1.0$ kcal $mol^{-1}$ (major to minor isomer) and $\Delta G^\ddagger = 9.8 \pm 1.0$ kcal $mol^{-1}$ (minor to major isomer) for *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$.

It appeared that a similar dynamic process was occurring for *trans*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$, but on account of the relatively low concentration of this isomer no analysis was performed.[1c]

## Results and Discussion

$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$.—In order to have activation parameters measured under the same conditions as used for the MeNC derivatives, $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ was re-examined in $CD_2Cl_2$. As previously demonstrated, $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ exists in solution as a mixture of *cis* and *trans* isomers.[8]

The 100.62 MHz $^{13}C$ NMR spectrum of *trans*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ shows an averaged CO signal in $CD_2Cl_2$ at δ 241.20 at −50 °C. On cooling to −61 °C this signal broadens to 78 Hz, while the linewidth of the corresponding $\eta^5\text{-}C_5H_5$ carbon signal is 14.5 Hz. On further cooling the carbonyl signal broadens further and vanishes. The extra 63.5 Hz broadening is attributed to exchange broadening from terminal ⟷ bridge exchange. If it is assumed that the $^{13}CO$ chemical shifts for the *trans* isomer are the same as for the *cis* isomer, then the chemical shift difference is 61.8 ppm, or 6218 Hz, from which can be estimated $\Delta G^\ddagger{}_{212} = 6.5$ kcal $mol^{-1}$. This assumption about the

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† *Non-SI unit employed:* cal = 4.184 J.

**Table 1** Assignment of the $^1H$ NMR chemical shifts of $[Fe_2(\eta^5-C_5H_5)_2(CO)_{4-n}(CNMe)_n]$, $n$ = 0–2, in $CD_2Cl_2$

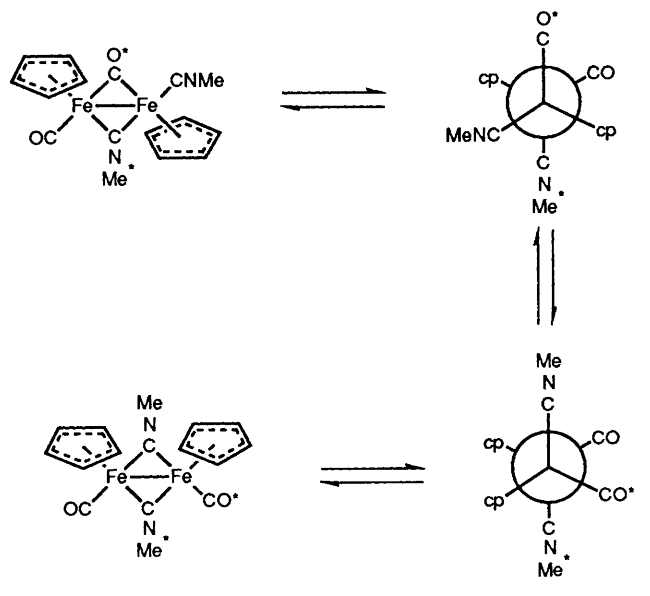
| Compound | $T$/°C | cp | μ-Me | Me |
|---|---|---|---|---|
| *cis*-$[Fe_2(\eta^5-C_5H_5)_2(CO)_4]$ | −72 | 4.82 | | |
| *trans*-$[Fe_2(\eta^5-C_5H_5)_2(CO)_4]$ | −72 | 4.73 | | |
| *cis*-$[Fe_2(\eta^5-C_5H_5)_2(\mu-CO)_2(CO)(CNMe)]$ **1** | −20 | 4.57<br>4.70 | | 2.95 |
| *cis*-$[Fe_2(\eta^5-C_5H_5)_2(\mu-CO)(CO)_2(\mu-CNMe)]$ **2** | −20 | 4.84 | 3.68 | |
| *trans*-$[Fe_2(\eta^5-C_5H_5)_2(CO)_3(CNMe)]$ **3**/**4** | −20 | 4.57[a] | 3.23[b] | 3.23[b] |
| *cis*-$[Fe_2(\eta^5-C_5H_5)_2(\mu-CO)(CO)(\mu-CNMe)(CNMe)]$ | 20 | 4.57<br>4.71 | 3.71 | 2.90 |
| *cis*-$[Fe_2(\eta^5-C_5H_5)_2(CO)_2(\mu-CNMe)_2]$ | 20 | 4.84 | 3.65 | |

[a] Obscured. Probable position. [b] Averaged.

**Table 2** Assignment of the $^{13}C$ chemical shifts of $[Fe_2(\eta^5-C_5H_5)_2(CO)_{4-n}(CNMe)_n]$, $n$ = 0–2, in $CD_2Cl_2$

| Compound | μ-CO | CO | μ-CN | CN | cp | μ-Me | Me |
|---|---|---|---|---|---|---|---|
| *cis*-$[Fe_2(\eta^5-C_5H_5)_2(CO)_4]$[a] | 271.92 | 210.12 | | | 87.68 | | |
| *trans*-$[Fe_2(\eta^5-C_5H_5)_2(CO)_4]$[a] | 241.20[b] | 241.20[b] | | | 89.01 | | |
| *cis*-$[Fe_2(\eta^5-C_5H_5)_2(\mu-CO)_2(CO)(CNMe)]$ **1**[c] | 280.45 | 212.91 | | 158.89 | 85.83<br>86.83 | | 30.05 |
| *cis*-$[Fe_2(\eta^5-C_5H_5)_2(\mu-CO)(CO)_2(\mu-CNMe)]$ **2**[c] | *d* | 211.11 | 247.64 | | 86.94 | 46.19 | |
| *trans*-$[Fe_2(\eta^5-C_5H_5)_2(CO)_3(CNMe)]$ **3**/**4**[c] | *d* | *d* | *d* | *d* | 88.02 | *d* | *d* |
| *cis*-$[Fe_2(\eta^5-C_5H_5)_2(\mu-CO)(CO)(\mu-CNMe)(CNMe)]$[e] | 281.20 | 213.78 | 259.03 | 163.10 | 86.16<br>85.54 | 46.21 | 29.97 |
| *cis*-$[Fe_2(\eta^5-C_5H_5)_2(CO)_2(\mu-CNMe)_2]$[e] | | 212.27 | 249.91 | | 86.46 | 45.98 | |

[a] At −60 °C. [b] Averaged. [c] At −20 °C. [d] Not observed. [e] At 0 °C.



**Scheme 2** The mechanism proposed by Adams and Cotton[1b] to account for the interchange of *cis*-$[Fe_2(\eta^5-C_5H_5)_2(CO)_2(\mu-CNMe)_2]$ and *trans*-$[Fe_2(\eta^5-C_5H_5)_2(\mu-CO)(CO)(\mu-CNMe)(CNMe)]$

chemical shifts is consistent with the average chemical shift for the *cis*-carbonyls being 241.0 ppm, very close to the chemical shift for the average carbonyls of the *trans* isomer. This value of $\Delta G^\ddagger$ can be compared with the literature value of 7.5 kcal mol$^{-1}$ which was measured in $CHCl_2F$ at 22.6 MHz.[9]

The *cis* ⟷ *trans* isomerism was also examined using line broadening of the cyclopentadienyl signals and $\Delta G^\ddagger$ is 12.1 kcal mol$^{-1}$. The corresponding literature value is 12.4 kcal mol$^{-1}$, measured in $CHCl_2F$.[8]

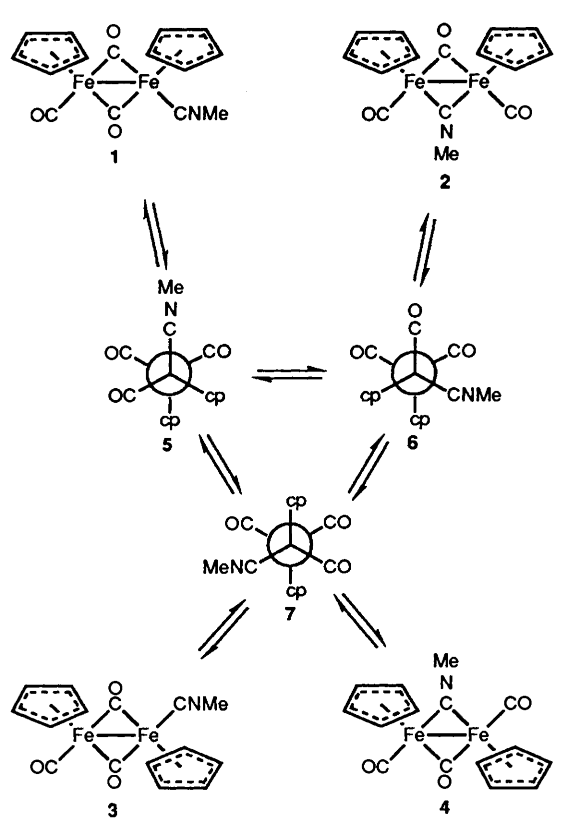
The $^1H$ NMR chemical shifts are given in Table 1 and the $^{13}C$ chemical shifts in Table 2.

Comparison of the $^{13}C$ NMR chemical shift of the μ-CO of *cis*-$[Fe_2(\eta^5-C_5H_5)_2(CO)_4]$ at δ 271.92 with those of the corresponding carbonyls of *cis*-$[Fe_2(\eta^5-C_5H_5)_2(\mu-CO)_2(CO)(CNMe)]$ at δ 280.45 and *cis*-$[Fe_2(\eta^5-C_5H_5)_2(\mu-CO)(CO)(\mu-CNMe)(CNMe)]$ at δ 281.20 shows it is at lower frequency than might be expected. This is consistent with the proposal from IR data that $[Fe_2(\eta^5-C_5H_5)_2(CO)_4]$ exists in solution as a mixture of bridge-opened and -closed isomers.[10] If it is assumed that for the bridge-closed isomer, δ(μ-CO) is 280 and δ(σ-CO) is 210, then this predicts that *ca.* 12% of the *cis*-$[Fe_2(\eta^5-C_5H_5)_2(CO)_4]$ is present in the bridge-opened form. A similar calculation may be applied to *trans*-$[Fe_2(\eta^5-C_5H_5)_2(CO)_4]$, where the averaged signal of δ 241.20 corresponds to a chemical shift of the μ-CO of δ 272.4 if δ(σ-CO) is assumed to be 210. Following the same treatment as applied to the *cis* isomer, this predicts that *ca.* 11% of the *trans*-$[Fe_2(\eta^5-C_5H_5)_2(CO)_4]$ is present in the bridge-opened form.

$[Fe_2(\eta^5-C_5H_5)_2(CO)_3(CNMe)]$.—The introduction of a CNR group into $[Fe_2(\eta^5-C_5H_5)_2(CO)_4]$ increases the number of possible isomers from two to four, **1**–**4**. This can be easily seen by considering the bridge-opened forms and the resulting bridge-closed species, see Scheme 3.

The investigation of $[Fe_2(\eta^5-C_5H_5)_2(CO)_4]$ has established that the opening of a $(\mu-CO)_2$ bridge is easy, and is fast at −60 °C, but that rotation about the Fe–Fe bond in the bridge-opened form is slow at −60 °C. There is no reason to suspect that this will be substantially different in $[Fe_2(\eta^5-C_5H_5)_2(CO)_3(CNMe)]$. However, we do not know the ease of opening of a (μ-CNMe)(μ-CO) bridge, which could be slow at −60 °C. Indeed, Adams and Cotton[1b] proposed for $[Fe_2(\eta^5-C_5H_5)_2(CO)_2(CNMe)_2]$ that the opening of a $(\mu-CNMe)_2$ bridge has a $\Delta G^\ddagger$ = 17.5 kcal mol$^{-1}$. On this basis, as the interconversion of isomers **5**–**7** by Fe–Fe bond rotation is slow at −60 °C, the observation of separate signals for **1**, **2** and **3**/**4** is to be expected. No prediction can be made about the ease of interconversion of **3** and **4**.

The presence of a bridging isocyanide in isomers **2** and **4** presents an additional complication. Bridging isocyanides are bent. In **2** and **4** this does not produce additional isomers, but does lower the symmetry of the molecules producing inequivalent cyclopentadienyl and terminal carbon groups, but it does not increase the number of methyl signals in the $^1H$ NMR spectrum. Examination of the variable-temperature $^1H$ NMR spectrum of $[Fe_2(\eta^5-C_5H_5)_2(CO)_3(CNMe)]$ shows that



Scheme 3 The isomers of $[Fe_2(\eta^5-C_5H_5)_2(CO)_3(CNMe)]$ and their interconversion

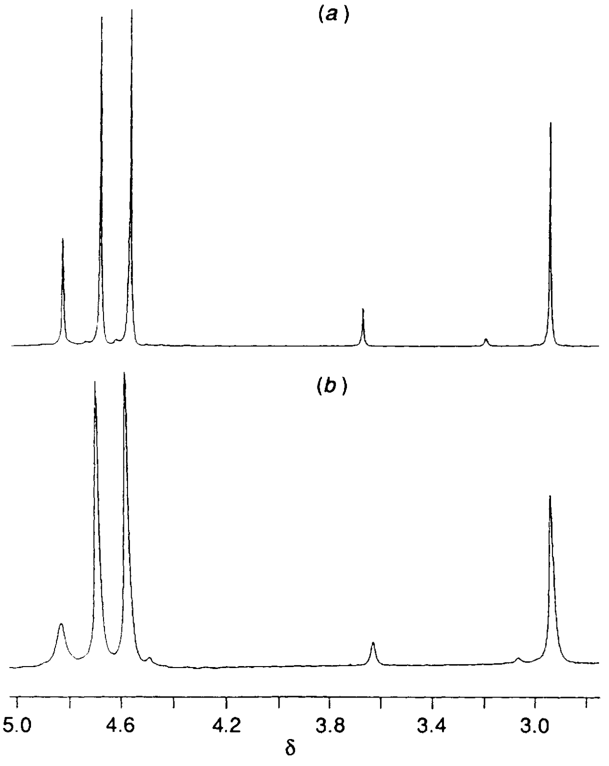


**Fig. 1** The 400.13 MHz $^1H$ NMR spectra of $[Fe_2(\eta^5-C_5H_5)_2(CO)_3(CNMe)]$ in $CD_2Cl_2$ at (*a*) 243 and (*b*) 183 K

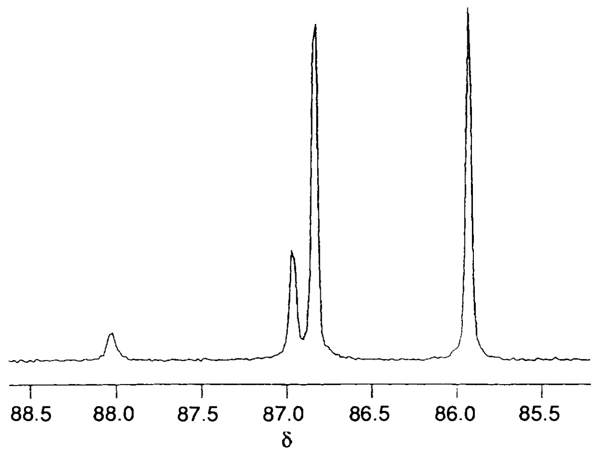


**Fig. 2** The 100.62 MHz $^{13}C$ NMR spectra of cyclopentadienyl signals of $[Fe_2(\eta^5-C_5H_5)_2(CO)_3(CNMe)]$ at 223 K

there are three methyl signals at 243 K at δ 3.70, 3.23 and 2.97, see Fig. 1(*a*). On cooling, the signal at δ 3.23 broadens, and at 183 K a new peak appears at δ 3.06, while the other two methyl signals do not change significantly, see Fig. 1(*b*). There is always a danger that the compound is impure, and the three methyl signals at 243 K arise from two or more compounds. This possibility was eliminated by using magnetisation transfer. A selective π pulse was applied to each of the three methyl signals in turn, and magnetisation transfer to the other two signals monitored as a function of time. This experiment unambiguously demonstrated that the three methyl signals at δ 3.70, 3.23 and 2.97 at 243 K arise from three interconverting isomers. The chemical shift of δ 3.70 is consistent with a bridging CNMe group, and that at δ 2.97 is consistent with a terminal CNMe group. The behaviour of the peak at δ 3.23 is consistent with a CNMe group exchanging between two environments. On cooling below 213 K this signal broadens and on further cooling to 193 K a peak appears at δ 3.06. There should be a second peak at *ca.* δ 3.7 with which the signal exchanges to give an averaged signal at δ 3.23 at 243 K. Presumably this signal is obscured by the strong signal at δ 3.70. This behaviour is consistent with Scheme 3. The signal at δ 3.70 at 243 K is assigned to **2**, that at δ 2.97 to **1**, and that at δ 3.23 to a rapidly interconverting mixture of **3** and **4**. On cooling to 193 K the interconversion of **3** and **4** becomes slow. The signal at δ 3.06 is due to **3**, while the signal due to **4** is obscured by the signal due to **2**. If it is assumed that **4** does have a chemical shift of δ 3.70 at 243 K, and the chemical shift of **3** is temperature independent, then the ratio of **3**:**4** at 243 K can be calculated from the average chemical shift, δ 3.23, as 2.8:1. The ratio of concentrations of **1**:**2**:(**3** + **4**) was obtained from integration of the methyl signals at 243 K as 4.7:1.0:0.43. Combining this with the estimated ratio of concentrations of **3**:**4** gives a ratio of concentrations of **1**:**2**:**3**:**4** as 4.7:1.0:0.31:0.11. This conclusion is in agreement with previous IR studies which concluded that all four isomers are present in solution.[1d]

The cyclopentadienyl $^1H$ and $^{13}C$ NMR signals are completely consistent with this interpretation, see Table 1. The presence of a third cyclopentadienyl signal is observed in the $^{13}C$ NMR spectrum, see Fig. 2. As with the $^1H$ NMR spectrum, there is the danger that an impurity gives rise to the weak signal at δ 88.02, but exchange spectroscopy (EXSY) at −22 °C showed exchange between this signal and the other cyclopentadienyl signals.

Quantitative measurements were performed using selective population inversion of the methyl signals in the $^1H$ NMR spectrum at −23.8 °C. In this experiment a selective 180° pulse was applied to one methyl signal. After a short delay a general 90° pulse was applied to determine where the exchange had occurred. The experiment was repeated for each methyl signal, using a number of different delays. The data were analysed quantitatively, as previously described.[11] The data, analysed including exchange between isomers **1** and **2**, yielded a least-squares error of 0.316 and $k_{12} = 0.11\ s^{-1}$. The data were then re-analysed with the constraint that $k_{12} = 0\ s^{-1}$, yielding the rate

**Table 3** Rate-constant matrix for the interconversion of the isomers **1**, **2** and **3**/**4**, assuming that $k_{12} = 0\ \mathrm{s^{-1}}$. The rates are in $\mathrm{s^{-1}}$

| | **2** | **3/4** | **1** |
|---|---|---|---|
| **2** | — | 2.49 | 0.00 |
| **3/4** | 1.06 | — | 1.88 |
| **1** | 0.00 | 20.9 | — |

**Table 4** Activation energies for the interconversion of isomers of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(CNMe)]$

| Reaction | $\Delta G^{\ddagger}$/kcal mol$^{-1}$ |
|---|---|
| $1 \longrightarrow 3/4$ | 14.2 |
| $2 \longrightarrow 3/4$ | 14.5 |
| $3/4 \longrightarrow 1$ | 13.0 |
| $3/4 \longrightarrow 2$ | 14.1 |
| $3 \longrightarrow 4$ | 9.4 |
| $4 \longrightarrow 3$ | 9.1 |

constant matrix in Table 3. The data yielded a least-squares error of 0.347. The introduction of a zero rate between **1** and **2** has not produced a substantially worse fit. The rates in Table 3 and Scheme 3 can be understood in terms of steric bulk. The direct interconversion of **1** and **2** requires the two cyclopentadienyl groups to pass each other. This will be sterically difficult, and is therefore a high-energy, slow process. The relative rates of exchange between **1** and **3**/**4**, and **2** and **3**/**4** reflect the relative sizes of the CO and CNMe groups. The exchange of **2** and **3**/**4** requires the large cyclopentadienyl group to pass the intermediate-size CNMe, while the exchange of **1** and **3**/**4** only requires the large cyclopentadienyl group to pass the small-size CO group, and is consequently faster.

The $^1H$ NMR spectra of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(CNMe)]$ show that the methyl signal due to isomers **3** and **4** broadens at $-54$ °C, and at $-84$ °C a separate broad methyl signal is observed for **3**. This signal can be used to calculate $\Delta G^{\ddagger}$ for exchange between **3** and **4**. The linewidth is *ca.* 15 Hz, hence $k = 47\ \mathrm{s^{-1}}$ and $\Delta G^{\ddagger} =$ *ca.* 9.4 kcal mol$^{-1}$ for the isomerism of **3** into **4**.

It has been earlier shown that isomers **3** and **4** are in a ratio of 2.8 : 1, corresponding to a $\Delta G^{\circ}$ of 0.38 kcal mol$^{-1}$. The activation energies for these processes are collected in Table 4. We believe that this is the first determination of the activation energy for the opening of a bridge containing a $\mu$-CNR group. There are some observations of this process in the literature,[12,13] but they involve intermediates of unknown stability. Comparison of the activation energy for ($\mu$-CO)($\mu$-CNMe) bridge opening in *trans*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2(\mu\text{-}CNMe)]$ **4** of 9.1 kcal mol$^{-1}$ with $(\mu\text{-}CO)_2$ bridge opening in *trans*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ of 6.5 kcal mol$^{-1}$ shows that the introduction of a $\mu$-CNMe group increases the activation energy for bridge opening.

$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$.—Previous work by Adams and Cotton[1b] has established that $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ exists in solution as a mixture of two isomers, $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$ and $[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$. There were some anomalies in their analysis, but most of these were clarified by a subsequent analysis of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(CNBu^t)_2]$.[3] Adams and Cotton suggested that the two isomers are *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$ and *trans*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$. The argument in favour of the *cis* structure for $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$ was based on the determination of the crystal structure.[2] The argument in favour of the *trans* structure for $[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$ was based on bridge opening to give $[\{Fe(\eta^5\text{-}C_5H_5)(CO)(CNMe)\}_2]$, where Fe–Fe bond rotation can only convert *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$ into *trans*- and not *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$. These isomers are related by the *racemic* set of bridge-opened isomers. According to Adams and Cotton, none of the corresponding set of isomers derived from the *meso* set of bridge-opened isomers is observed.

There are several major weaknesses in Adams and Cotton's assignment of the *trans* configuration to $[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$ (*a*) It has been established that the *cis*–*trans* ratio of isomers for $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ is markedly solvent dependent, see Table 5. This marked solvent dependence is not found for the two isomers of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$.

(*b*) The Adams and Cotton assignment requires that the opening of a ($\mu$-CO)($\mu$-CNMe) bridge in $[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$ has an activation energy of 17.5 kcal mol$^{-1}$, see Scheme 1, rather than the 9.1 and 9.4 kcal mol$^{-1}$ reported here for *trans*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2(\mu\text{-}CNMe)]$. The 17.5 kcal mol$^{-1}$ barrier is consistent with the barrier for rotation about the Fe–Fe bond, see below.

(*c*) The interconversion of *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$ and *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$ can be achieved *via* a $[(OC)_2(\eta^5\text{-}C_5H_5)Fe\text{–}Fe(\eta^5\text{-}C_5H_5)(CNMe)_2]$ intermediate which provides a link between the *meso* and *racemic* sets of complexes. The presence of this intermediate was not considered by Adams and Cotton, but their mass spectroscopic data show the presence of a major (51%) ion due to $[Fe(\eta^5\text{-}C_5H_5)(CNMe)_2]^+$ and a subsequent crystal structure of $[Fe_3(CO)_{10}(CNBu^t)_2]$ has shown that two isocyanide ligands can occur on one iron atom, even where there is a choice of three iron atoms.[14] Consequently $[(OC)_2(\eta^5\text{-}C_5H_5)Fe\text{–}Fe(\eta^5\text{-}C_5H_5)(CNMe)_2]$ must be considered to be a viable intermediate.[1a] A similar suggestion has been made previously to account for the fluxionality of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(CNBu^t)_2]$.[3]

It is therefore far more probable that the two isomers observed for $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$ are *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$ and *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$ NOT *trans*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$. It is then possible to give a consistent picture of the dynamic processes occurring in these molecules. The higher-energy process, reported by Adams and Cotton, interconverts *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$ and *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$ *via* $[(OC)_2(\eta^5\text{-}C_5H_5)Fe\text{–}Fe(\eta^5\text{-}C_5H_5)(CNMe)_2]$ and *trans*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$ intermediates with $\Delta G^{\ddagger} = 18.9$ kcal mol$^{-1}$.

*Comparison of the Activation Parameters of* $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$.—It has been shown that the activation energy for bridge opening increases on going from a $(\mu\text{-}CO)_2$ to a ($\mu$-CO)($\mu$-CNMe) bridge. It is to be anticipated that the activation energy for the opening of a $(\mu\text{-}CNMe)_2$ bridge will be higher still. Most of the dynamic processes which have been quantified in this and previous work for $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ have involved two dynamic processes, bridge opening and rotation about the Fe–Fe bond. It is not possible to separate reliably the activation energies for these two processes, but the activation energy increases from *ca.* 12 kcal mol$^{-1}$ when $n = 0$, to *ca.* 14 kcal mol$^{-1}$ when $n = 1$, and to *ca.* 18 kcal mol$^{-1}$ when $n = 2$. No value has been reported when $n = 3$ or 4, but when $n = 3$ the NMR spectrum shows separate $\mu$-CNMe and $\sigma$-CNMe signals at room temperature[1a] implying that the activation energy is greater than 18 kcal mol$^{-1}$, and when $n = 4$ it has been proposed that *cis*- and *trans*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(CNMe)_4]$ can be separated,[15] implying that the activation energy is greater than 25 kcal mol$^{-1}$. These observations are consistent with an increase in activation energy on going from a $(\mu\text{-}CO)_2$ to ($\mu$-CO)($\mu$-CNMe) bridge and then to a $(\mu\text{-}CNMe)_2$ bridge. In addition, a CNMe ligand is sterically larger than a CO ligand, causing steric barriers to rotation of the Fe–Fe bond in the bridge-opened form. This behaviour is

**Table 5** The solvent dependence of the ratio of concentrations of isomers of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ at −60 °C and $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ at 20 °C

| Solvent | *cis*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$: *trans*-$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ | $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$: $[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)(\mu\text{-}CNMe)(CNMe)]$ |
|---|---|---|
| $CD_3C_6D_5$ | 1:2.08 | 1:1.10 |
| $CD_2Cl_2$ | 1:0.85 | 1:1.53 |
| $CDCl_3$ | 1:0.53 | 1:2.40 |
| $(CD_3)_2CO$ | 1:0.04 | 1:0.67 |

observed for the interconversion of the isomers of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(CNMe)]$, see Scheme 3. Interconversion of isomers **1** and **3**/**4** requires bridge opening to **5**, rotation to **7**, eclipsing CO/cp (twice) and CO/CNMe, followed by bridge closure to **3** or **4**. Interconversion of **2** and **3**/**4** requires bridge opening to **6**, rotation to **7**, eclipsing CNMe/cp, CO/cp and CO/CO, followed by bridge closure to **3** or **4**. Interconversion of **1** and **2** requires bridge opening to **5**, rotation to **6**, eclipsing cp/cp, CO/CNMe and CO/CO, followed by bridge closure to **2**. On the basis of size, the steric repulsions will follow the order cp/cp > CNMe/cp > CO/cp > CO/CNMe > CO/CO. On this basis the rotation barriers should be in the order **5** ⟷ **6** > **6** ⟷ **7** > **5** ⟷ **7**, and it is this order that is found, see Table 4.

## Experimental

The compounds were prepared according to the literature.[1] The NMR spectra were measured using a Bruker WH400 spectrometer. The temperatures were calibrated using a Comark digital electronic thermometer with a Cu/Cu–Ni thermocouple in an NMR tube containing $CH_2Cl_2$.

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