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C–C Bond Cleavage

Comparative Studies of Thermally Induced Homolytic Carbon–Carbon Bond Cleavage Reactions of Strained Dicarba[2]ferrocenophanes and Their Ring-Opened Oligomers and Polymers

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Abstract: Reactivity studies of dicarba[2]ferrocenophanes and also their corresponding ring-opened oligomers and polymers have been conducted in order to provide mechanistic insight into the processes that occur under the conditions of their thermal ring-opening polymerisation (ROP) (300 °C). Thermolysis of dicarba[2]ferrocenophane *rac*-[Fe(η^5-C_5H_4)$_2$(CHPh)$_2$] (*rac*-**14**; 300 °C, 1 h) does not lead to thermal ROP. To investigate this system further, *rac*-**14** was heated in the presence of an excess of cyclopentadienyl anion, to mimic the postulated propagating sites for thermally polymerisable analogues. This afforded acyclic [(η^5-C_5H_5)Fe(η^5-C_5H_4)-CH_2Ph] (**17**) through cleavage of both a Fe–Cp bond and also the C–C bond derived from the dicarba bridge. Evidence supporting a potential homolytic C–C bond cleavage pathway that occurs in the absence of ring-strain was provided through thermolysis of an acyclic analogue of *rac*-**14**, namely [(η^5-C_5H_5)Fe(η^5-C_5H_4)(CHPh)$_2$-C_5H_5] (**15**; 300 °C, 1 h), which also afforded ferrocene derivative **17**. This reactivity pathway appears general for post-ROP species bearing phenyl substituents on adjacent carbons, and consequently was also observed during the thermolysis of linear polyferrocenylethylene [Fe(η^5-C_5H_4)$_2$(CHPh)$_2$]$_n$ (**16**; 300 °C, 1 h), which was prepared by photocontrolled ROP of *rac*-**14** at 5 °C. This afforded ferrocene derivative [Fe(η^5-$C_5H_4CH_2Ph$)$_2$] (**23**) through selective cleavage of the –H(Ph)C–C(Ph)H– bonds in the dicarba linkers. These processes appear to be facilitated by the presence of bulky, radical-stabilising phenyl substituents on each carbon of the linker, as demonstrated through the contrasting thermal properties of unsubstituted linear trimer [(η^5-C_5H_5)Fe(η^5-C_5H_4)(CH_2)$_2$(η^5-C_5H_4)Fe(η^5-C_5H_4)(CH_2)$_2$(η^5-C_5H_4)Fe(η^5-C_5H_5)] (**29**) with a –H_2C–CH_2– spacer, which proved significantly more stable under analogous conditions. Evidence for the radical intermediates formed through C–C bond cleavage was detected through high-resolution mass spectrometric analysis of co-thermolysis reactions involving *rac*-**14** and **15** (300 °C, 1 h), which indicated the presence of higher molecular weight species, postulated to be formed through cross-coupling of these intermediates.

Introduction

Strained [*n*]metallocenophanes **1** are a broad class of cyclic organometallic species that have received significant attention since the first example was reported in 1960.[1] The expanding field of [*n*]metallocenophane chemistry has been facilitated through the ability to vary both the central metal atom and bridging moiety, allowing a wide variety of these species to be realised,[2] including those of Fe,[3] Ru,[4] Co,[5] Ni[6] and Mo,[7] in addition to analogous species containing other π-hydrocarbon ligands.[8] Computational studies indicate that [*n*]metallocenophanes containing more than four d electrons possess substantial ring-strain upon tilting of the cyclopentadienyl (Cp) ligands away from their preferred parallel conformation,[9] as defined quantitatively by the angle α, along with the other structural distortions illustrated (Figure 1).

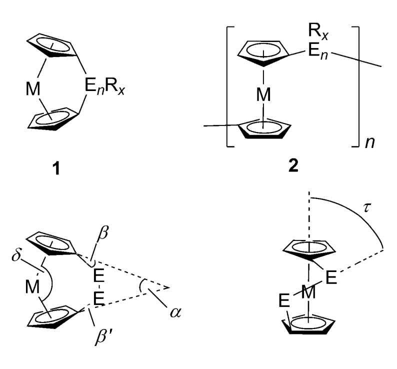

Figure 1. Structural metrics for [*n*]metallocenophanes.

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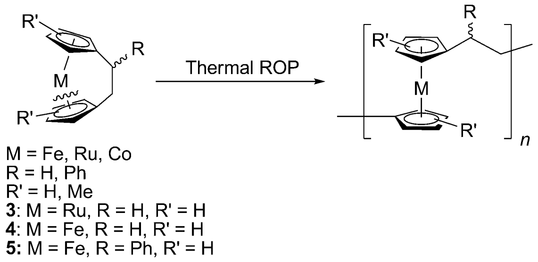
Consequently, when the ansa bridge is suitably short ($n \leq 2$) affording a substantial tilt angle ($\alpha = 14–33°$), the inherent ring-strain can be exploited in ring-opening reactions including, most significantly, ring-opening polymerisation (ROP).[10] ROP provides access to metallopolymers **2** that incorporate metallocene (or related) units in the main chain. To date, these materials have attracted attention for a variety of applications, including uses as etch resists,[11] catalytic and magnetic ceramic precursors,[12] redox-active microcapsules and microspheres,[13] the redox-active component of photonic crystal displays,[14] and as self-assembled, nanostructured materials.[15]

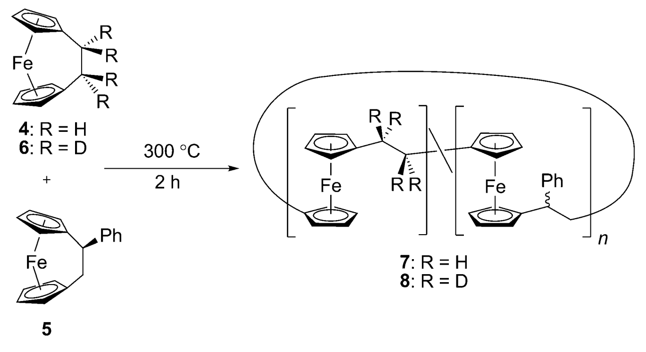
Dicarba[2]metallocenophanes **1** (M = Fe, Ru, Co; $E_nR_x = C_2R_4$) are a subclass of [*n*]metallocenophanes that display diverse reactivity including thermal ROP,[16] photolytic ROP through cleavage of the M–Cp bond,[17] and (for species **3**) metal–metal bond formation upon oxidation, affording a dicarba[2]ruthenocenophanium dimer.[18]

Studies on the thermal ROP of dicarba[2]ferrocenophanes **4** and **5** have indicated that the resulting cyclic polyferrocenylethylenes have moderate molecular weight ($M_w = 4800–96\,000$ Da) and broad distributions (PDI = 1.1–3.6; Scheme 1).

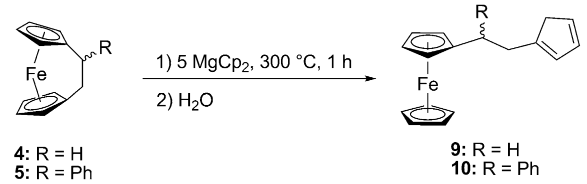


Scheme 1. Thermal ROP of dicarba[2]metallocenophanes.

Insight into the mechanism was achieved through comparative NMR spectroscopic analysis of random copolymer **7** with the deuterated analogue **8** (Scheme 2).[19] The absence of NMR signals which could be assigned to a $-CH(Ph)CD_2-$ linker in **8** indicated that a mechanism of thermal ROP based upon homolytic C–C bridge bond cleavage was improbable. In addition, trapping of the ring-opened monomeric species **9** and **10** by a thermolysis reaction (300 °C, 1 h) in the presence of an excess of $MgCp_2$, confirmed that the Fe–Cp bond could be cleaved heterolytically under the conditions employed in thermal ROP, suggesting that propagation likely proceeds through this mechanism (Scheme 3).

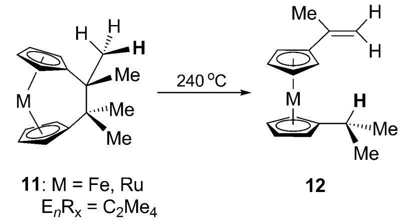


Scheme 2. Random thermal copolymerisations of dicarba[2]ferrocenophane **5** with either **4** and **6**, respectively.

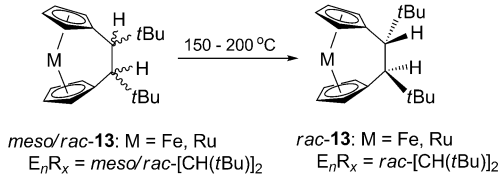


Scheme 3. Thermal ring-opening reactions of dicarba[2]ferrocenophanes **4** and **5** in the presence of an excess of $MgCp_2$.

In contrast to **4** and **5**, species **11** and *meso/rac*-**13** undergo either radical disproportionation, to afford substituted ferrocene **12**, or isomerisation, to yield the thermodynamically more stable *rac*-**13** isomer, respectively (Scheme 4 and Scheme 5).[20] The preferred reactivity pathway is dependent on the presence or absence of hydrogen substituents at the carbon in the α position respective to the dicarba bridge.



Scheme 4. Thermally induced radical disproportionation of dicarba[2]metallocenophanes.



Scheme 5. Thermally induced isomerisation of dicarba[2]metallocenophanes.

These results indicate that an interesting structure–thermal reactivity relationship exists for dicarba[2]ferrocenophanes. Thus, species bearing either zero or one non-hydrogen substituents on the dicarba bridge undergo thermal ROP by Fe–Cp bond cleavage. Alternatively, species bearing an equal number of non-hydrogen substituents undergo homolytic C–C bridge bond cleavage, followed by radical disproportionation or isomerisation.

In order to provide further insight into the reaction pathways that take place under thermal polymerisation conditions for dicarba[2]ferrocenophanes, we now report thermal reactivity studies of a diphenyl-substituted dicarba[2]ferrocenophane *rac*-**14** [M = Fe, E_nR_x = *rac*-$(CHPh)_2$], its ring-opened analogue (**15**) and linear polyferrocenylethylene $[Fe(\eta^5\text{-}C_5H_4)_2(CHPh)_2]_n$

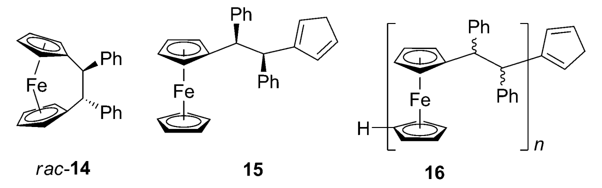
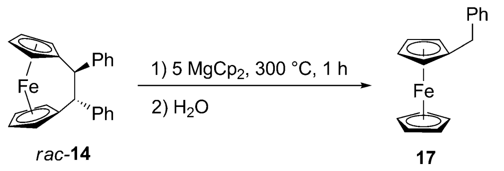


Figure 2. Dicarba[2]ferrocenophane *rac*-14, acyclic analogue **15** and polyferrocenylethylene **16**.



Scheme 6. Thermolysis of dicarba[2]ferrocenophane *rac*-**14** in the presence of excess $MgCp_2$.[24]

(**16**; Figure 2). The potential for coupling reactions of the radical intermediates formed during thermally induced, homolytic cleavage of the dicarba bridges and spacers has also been explored.

Results and Discussion

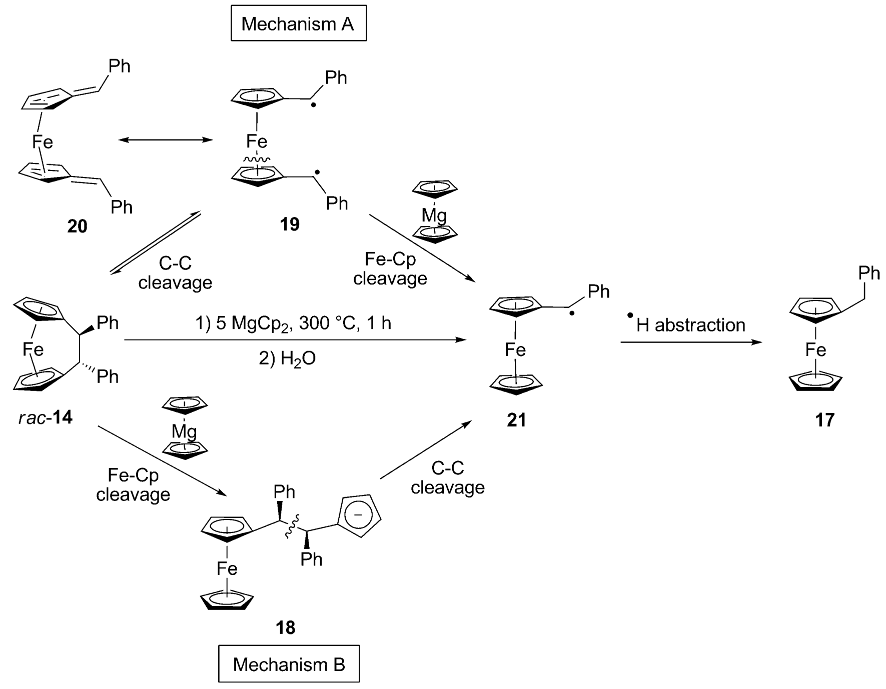
Investigations into the thermal lability of the –H(Ph)C–C(Ph)H– bond in the presence and absence of ring-strain

Thermal reactivity of *rac*-14, and ring-opened species 15 a and 15 b: Our first experiments aimed to extend the studies used to elucidate the mechanism of the thermal ROP of dicarba[2]ferrocenophanes to other strained dicarba[2]ferrocenophanes that do not polymerise.[21] As noted above, we have previously shown that thermolysis (300 °C, 1 h) of thermally polymerisable metallocenophanes **4** and **5** in the presence of a large excess of $MgCp_2$ yields the ring-opened monomeric analogues **9** and **10** by cleavage of the Fe–Cp bond (Scheme 3). In contrast, when we heated thermal ROP-resistant *rac*-**14** under identical reaction conditions, the only product successfully isolated was ferrocene derivative **17** in a moderate yield (50 %; Scheme 6). NMR spectroscopic analysis of the reaction mixture indicated that no starting material remained following the reaction.[22]

The microcrystalline yellow product **17** was characterised by both ^{1}H and ^{13}C NMR spectroscopy, which gave data consistent with previous reports describing the synthesis of **17** by reduction of a ferrocenyl benzyl alcohol precursor.[23] High and low-resolution MS data, in addition to elemental analysis, were obtained and were also found to be consistent with the assigned structure.

The observed reactivity differs from the thermolysis reaction of *meso/rac*-**14** alone at 300 °C, for which isomerisation by homolytic C–C bridge bond cleavage occurs, to afford the *rac*-**14** isomer exclusively. The distorted structure of *rac*-**14** [$\alpha = 22.7(3)^\circ$, C–C bridge = 1.572(3) Å],[17b] which has both an increased α angle and C–C bridge bond length relative to those reported for both **4** [$\alpha = 21.6(4)^\circ$, C–C bridge = 1.539(12) Å][16b] and **5** [$\alpha = 21.18(9)^\circ$, C–C bridge = 1.545(3) Å],[19] has previously been used as a rationale for the observed differences in reactivity. Thus, homolytic C–C bond cleavage of the C_2-bridge is detected for the former species and heterolytic Fe–Cp bond cleavage for the latter two ferrocenophanes.[19] However, in contrast to these previous studies, formation of **17** from *rac*-**14** and $MgCp_2$ at 300 °C is apparently facilitated through cleavage of both the C–C bond derived from the bridge and the Fe–Cp bond.

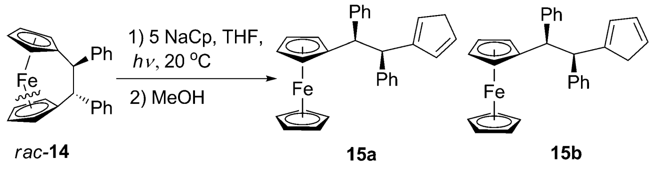
Two of the most likely mechanisms for the formation of **17** are shown in Scheme 7. Either of these processes could operate, or both may occur together. Homolytic cleavage of the C–C bridge bond could occur to afford diradical intermediate **19** (mechanism A), a process analogous to that postulated during the thermolysis of species similar to *rac*-**14**, such as **11** and *meso/rac*-**13**.[20] Computational studies of the diradical intermediate **19**, which results from homolytic C–C bridge bond cleavage,[25] suggest it exists as a resonance hybrid with an alternative resonance form consisting of Fe^0 bis-fulvenyl species



Scheme 7. Potential mechanisms of formation of monosubstituted ferrocene **17**.

20.[26] Nucleophilic attack on intermediate **19** could then afford **21**, which might abstract H$^\bullet$ to afford **17**. The alternative mechanism B involves heterolytic cleavage of the Fe–Cp bond in accordance with the observed reactivity discussed previously,[19] affording the ring-opened intermediate **18**. This intermediate could then undergo thermally induced C–C cleavage to also yield intermediate **21**.

To investigate the likelihood of the C–C bond cleavage process that occurs after ring-opening, in the absence of ring-strain (mechanism B), thermolysis of ring-opened species **15** was examined. To prepare this species, irradiation of dicarba[2]-ferrocenophane *rac*-**14** with Pyrex filtered UV light in the presence of five equivalents of NaCp (at 20 °C) was performed. This afforded the ring-opened product as a mixture of isomers (**15a** and **15b**) in good yield (69%; Scheme 8).

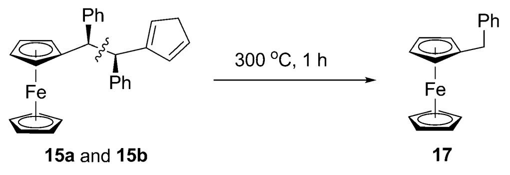


Scheme 8. Photolytic ring-opening of *rac*-**14** in the presence of excess NaCp.

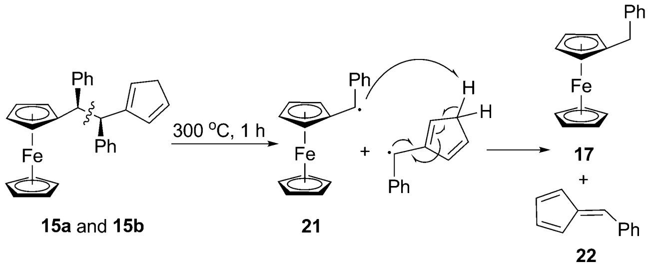
The two isomers (**15a** and **15b**) were isolated in a 1:1.3 ratio, and were confirmed through the identification of distinctive resonances in both the ^1H NMR spectrum (singlets at $\delta=3.74$ and 3.72 ppm assigned to the η^5-C_5H_5 groups of each isomer) and $^{13}C\{^1H\}$ NMR spectrum (signals at $\delta=93.5$ and 93.1 ppm assigned to the Cp_{ipso} carbons of each isomer). Unfortunately, all attempts to separate the isomers proved unsuccessful. Confirmation of the structure of **15** was also provided through elemental analysis and high-resolution MS. Low-resolution MS also identified the parent ion at 430.4 *m/z* (12%, M^+).

With compounds **15a** and **15b** in hand, the thermal stability of the dicarba spacer was then investigated. After 5 min at 300 °C **15a** and **15b** melted into a dark red, free-flowing fluid and remained in this state for the duration of the thermolysis experiment (1 h). Following work-up, **17** was isolated in high yield (91%; Scheme 9). The formation of **17** confirmed that the dicarba spacer, at least in species bearing phenyl substituents on both carbons, can be cleaved in the absence of ring-strain.

It is important to note that ^1H NMR spectroscopic analysis of the crude reaction mixture did not display any signals that could be assigned to a product derived from the $(C_5H_5)CH(Ph)$ fragment, expected to also form following cleavage of the –H(Ph)C–C(Ph)H– bond. Although the fate of this organic fragment is unknown, it is postulated that it is not stable at the elevated temperatures employed for the thermal bond cleavage reaction.[27] Indeed, a thermolysis reaction of **22**, synthesised through a previously published procedure,[28] confirmed its thermal instability with significant degradation occurring.[29] Further insight was obtained, however, through low-resolution MS studies of starting material **15** for which, in addition to a peak for **21** (275.2 *m/z*, 100%), a peak at 153.2 *m/z* (20%) assigned to the fulvene **22**–H, was observed (Figure S1 in the Supporting Information). Fragment **22** presumably loses H during the MS analysis. Thus, a mechanism for the thermal degradation of **15a** and **15b** was postulated whereby, upon thermolysis, the C–C spacer cleaves, affording radical intermediate **21**, which abstracts H$^\bullet$ from the fragmented intermediate to afford species **17** and **22**, respectively (Scheme 10).[30]



Scheme 9. Thermolysis of **15a** and **15b** (only one isomer is shown) at 300 °C to afford **17**.



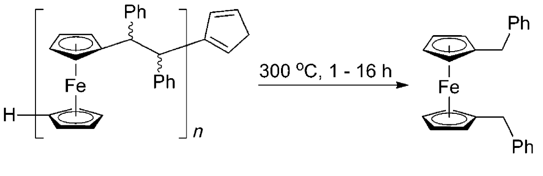
Scheme 10. Potential mechanism of formation for **17** and **22** (not observed).

The proposed mechanism of H$^\bullet$ transfer was investigated through deuterium labelling of the pendant Cp ring of **15a** and **15b**. NaOD in D_2O was added to a dioxane solution of **15a** and **15b** (for details see the Supporting Information). Upon work-up, deuteration to form $[D_5]$**15a** and $[D_5]$**15b** was confirmed through NMR spectroscopic analysis. Thus, characteristic signals between 6.65 and 5.90 ppm, assigned to the olefinic protons, and between 3.00 to 2.50 ppm, assigned to the CH_2 group of the pendant Cp ring, were observed in the ^2H NMR spectrum, and were absent from the ^1H NMR spectrum (Figure S2 in the Supporting Information).

Upon thermolysis of $[D_5]$**15a** and $[D_5]$**15b** (300 °C, 1 h), ^1H and ^2H NMR analysis revealed 38% incorporation of D onto the CH(Ph) group of the product (**17**; Figure S3 in the Supporting Information).[31] Confirmation was also provided through ^{13}C NMR spectroscopic analysis, which displayed a triplet at 36.2 ppm, with characteristic deuterium splitting, assigned to -*C*HD(Ph) carbon. These observations suggest that although the proposed mechanism does occur in the melt, other reactivity pathways are also operative. However, given the high reactivity of radical species, the reaction temperatures employed and the formation of other uncharacterised by-products, it is perhaps unsurprising that non-deuterated **17** is also a product from the thermolysis reaction.

Thermal reactivity of polyferrocenylethylene 16: To probe the potential of thermally induced carbon–carbon bond cleavage as a possible depolymerisation pathway, the thermal stability of polyferrocenylethylenes bearing phenyl substituents on adjacent carbons of the dicarba spacer was investigated. To this end, samples of linear polyferrocenylethylene **16** with a narrow molecular weight distribution ($M_w = 21\,800$, PDI = 1.21) were prepared by photocontrolled ROP (5 °C, one week).[17b] These were then thermolysed at 300 °C in evacuated thermolysis tubes for either 1 h (to give **16a**), 5 h (to give **16b**), or 16 h (to give **16c**). During each thermolysis reaction the mobility of the sample noticeably increased, consistent with depolymerisation of **16**. After each reaction the sample was dissolved in THF and filtered, upon which a small amount of black material was separated.[32]

Disubstituted ferrocene **23** was isolated from the mother liquors following precipitation of the residual polyferrocenylethylene (**16a–b**) or unidentified (**16c**) by-products from the crude reaction mixtures. The yield of **23** varied depending on the reaction time and was highest (68%) after a 5 h thermolysis experiment (Scheme 11).[33] ^{1}H NMR spectroscopy and high-resolution MS data for **23** were consistent with that reported when this species was previously synthesised by reduction of 1,1-dibenzoylferrocene.[34]



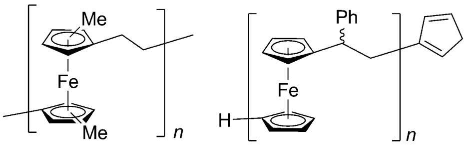
16 **23**

Scheme 11. Thermolysis of **16** ($M_w = 21\,800$ Da, PDI = 1.21) at 300 °C.

The radical intermediates formed during the thermal depolymerisation of **16** apparently abstract H$^•$ to afford **23**. Work-up of the thermolysis reactions of **16** (and **15a/b**) with deuterated solvent ($CDCl_3$) confirmed that H$^•$ is not derived from this source. Identical products were isolated, as confirmed by both NMR spectroscopic and mass spectrometric analysis of **23** (and **17**), respectively. For both **15a/b** and **16**, which are thermolysed alone, it can therefore be concluded that H$^•$ is likely provided by a C–C bond cleavage product. Radical coupling to reform the dicarba C–C bond to produce monomer *rac*-**14**, as observed during the previously reported thermal isomerisation of *meso/rac*-**14** to *rac*-**14**,[19] does not result from thermolysis of **16**. The differences in the products formed in each case can be rationalised through examination of the reactivity pathways. In the case of the thermolysis of *meso/rac*-**14**, cleavage of the dicarba bridge affords intermediate **19** (Scheme 7), with two radical CH groups in close proximity to each other which, following CpC–CH(Ph) bond rotation, can couple rapidly to reform the dicarba bridge and thus convert to the thermodynamically preferred *rac*-**14** isomer. However, for the depolymerisation of **16** to also afford *rac*-**14** as a product, two adjacent –H(Ph)C–C(Ph)H– bonds of the polymer backbone must break simultaneously to produce the same diradical intermediate (**19**). Furthermore, the intermediate formed from this process will presumably be in a conformation in which the two radical sites are approximately *trans* to one another. Given the high reactivity of radical species, coupled with the statistical improbability of two adjacent –H(Ph)C–C(Ph)H– bonds breaking simultaneously and combined with the need for rotation around the Fe–Cp bond to enable radical site proximity, it is not surprising that the thermolysis of **16** results in the formation of **23**, and not *rac*-**14**.

NMR spectroscopic and gel permeation chromatographic (GPC) analysis of polyferrocenylethyene samples **16a** (300 °C, 1 h) and **16b** (300 °C, 5 h) indicated that the product was of reduced molecular weight and increased polydispersity (PDI) relative to **16** ($M_w = 21\,800$ g mol^{-1}, PDI = 1.21; Figure S4 in the Supporting Information). Polymer **16b** ($M_w = 3600$ g mol^{-1}, PDI = 1.32) underwent a greater reduction in molecular weight than **16a** ($M_w = 6300$ g mol^{-1}, PDI = 1.76), suggesting that longer thermolysis times result in a greater reduction in the final molecular weight of the polymeric by-products.[35] Interestingly, ^{1}H NMR spectroscopic analysis of both **16a** and **16b** did not display any signals that could be assigned to the diene end group, which suggested that these moieties potentially participate in additional reactivity, or alternatively, are cleaved from the polymer backbone upon thermolysis. NMR spectroscopic characterisation of the residual species **16c**, isolated from the 16 h thermolysis experiment, was impeded by the presence of paramagnetic impurities.[36]

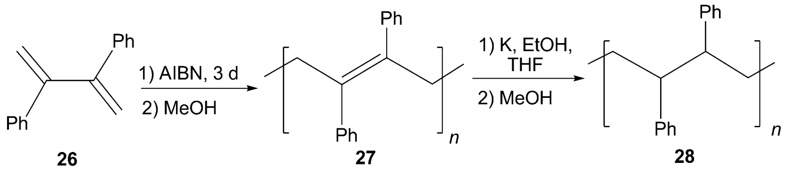
Cleavage of the –H(Ph)C–C(Ph)H– bonds in **16** results in significant depolymerisation, a result which is in contrast to previously reported thermolysis reactions (300 °C, 1 h) on cyclic polyferrocenylethylene **24**,[16b] bearing no non-hydrogen substitutents on the dicarba linker, and linear **25**,[19] bearing a phenyl substituent on only one carbon of the linker (Figure 3). In these examples, analysis of the thermolysed polymers indicated no significant change in the molecular weight for the former, and a slight increase in both the molecular weight and PDI in the case of the latter. The change in the observed M_w and PDI for **25** was postulated to result from either thermally induced branching, crosslinking, or reactivity of the diene end-group.[19]



24 **25**

Figure 3. Polyferrocenylethylenes **24** and **25**.

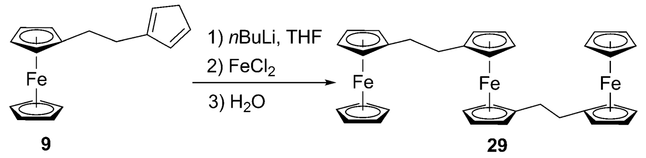
Few examples exist in the literature of polymers that contain bulky phenyl substituents on adjacent carbons of the backbone. Consistent with our observations, head-to-head polystyrene **28**, synthesised through the radical polymerisation of diphenyl butadiene,[37] undergoes thermally induced cleavage of



Scheme 12. Synthesis of head-to-head polystyrene **28**.[37]

the –H(Ph)C–C(Ph)H– bond at 280 °C, to afford a variety of products (Scheme 12).[38]

Thermolysis of unsubstituted linear trimer 29: To further explore the variation in the thermal stability of acyclic ferrocenylethylenes bearing different substituents on the dicarba linker, the linear trimer **29**, bearing no non-hydrogen substituents was prepared. This was achieved through reaction of **9**, prepared using a previously published protocol,[17a] with *n*BuLi and $FeCl_2$, affording the linear trimer **29** as a yellow powder in a good yield (78 %; Scheme 13).[39] Formation of trimer **29** allows the thermal stability of the dicarba bridge in the absence of non-hydrogen substituents to be ascertained, without the potential for additional reactivity pathways arising from cyclopentadiene end-group loss and C–C bond labilisation, as was observed during the thermolysis reactions of both **9**,[40] and polyferrocenylethylene **16**.



Scheme 13. Synthesis of linear trimer **29**.

The trimer **29** was characterised by NMR spectroscopy. The ^1H NMR spectrum displayed a distinctive singlet resonance at $\delta = 4.11$ ppm, assigned to the η^5-C_5H_5 groups, a multiplet at 4.07 and two broad singlets at 4.03 and 4.01 ppm assigned to the η^5-C_5H_4 groups and a singlet at 2.53 ppm assigned to the protons of the dicarba bridge. In addition, the trimer was analysed by high-resolution MS, which confirmed the presence of the trimer parent ion at 610.0707 *m/z*. The electrochemical properties of the trimer were also investigated, and found to be consistent with previous studies on analogous species (Figure S5 in the Supporting Information).[41a, 16b, 41b] Attempts to produce crystals suitable for X-ray crystallographic analysis, however, were unsuccessful.

The trimer **29** was thermolysed at 300 °C for 1 h. The sample melted to afford a viscous red material after 5 min, with no further change being observed for the remaining duration of the attempted thermolysis. Upon being cooled, the tube was opened in air and subsequent work-up gave an almost quantitative recovery (yield = 94 %) of unreacted **29** as identified by NMR spectroscopy and MS.[42] To observe the extent of the thermal stability of trimer **29**, a thermolysis experiment was conducted over an increased time period (5 h). Again, no products that would be expected to result from cleavage of the dicarba spacer were detected, although recovered starting material was obtained in a substantially decreased yield (26 %) as a result of the formation of metallic iron by-products. It appears that competing reactivity pathways are in operation under the thermolysis conditions employed, including thermal decomposition to afford metallic iron, which appears to be operative in all cases studied.[43] Significantly, under standard thermal ROP conditions the ligand framework of trimer **29** does not appear to undergo carbon–carbon bond cleavage to afford ferrocene based products.

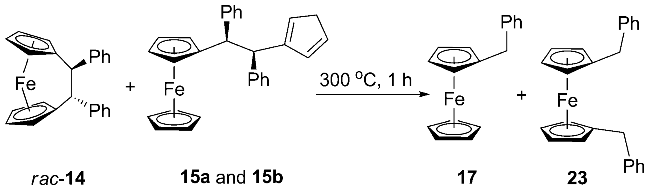
Interestingly, low-resolution MS analysis of **29**, which showed the presence of the trimer parent ion, also displayed additional peaks at *m/z* 333.1 (42 %, $M^+ - FeC_{17}H_{17}$) and 199.1 (100 %, $M^+ - Fe_2C_{23}H_{23}$). The peak at 333.1 was assigned to the $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)(CH_2)_2(\eta^5\text{-}C_5H_4)Fe^+]$ fragment, which results from cleavage of an Fe–Cp bond. Furthermore, the peak at 199.1 *m/z* was assigned to the $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)CH$ fragment believed to result from homolytic cleavage of the C–C spacer in trimer **29**. This latter observation suggests that MS analysis can induce homolytic cleavage of this bond although the conditions employed in the MS do not exceed temperatures of 200 °C (see the Supporting Information). It is possible that, once ionised under MS conditions, **29** can undergo more facile homolytic cleavage of the dicarba spacer than for the neutral species.

The relative thermal stability of **29** under the identical reaction conditions (300 °C, 1 h) employed to induce the carbon–carbon bond cleavage in **15** and **16** indicates that the presence of the bulky phenyl substituents on adjacent carbons of the dicarba bridge facilitates the selective cleavage of the –H(Ph)C–C(Ph)H– bond. Consistent with well-established precedent, the steric-strain, provided through the presence of phenyl substituents on adjacent carbons, acts to weaken the carbon–carbon bond.[44] In addition, the phenyl substituents can stabilise the radical intermediates that result from homolytic C–C bond cleavage through resonance effects. These contributing factors presumably facilitate the observed carbon–carbon bond cleavage under the thermolysis conditions employed and, importantly, allow the conclusion to be made that in these and the previous studies discussed, ring-strain *is not* a requirement for this process.

Cross-coupling reactions of radical intermediates

Trapping of the postulated radical intermediates in the aforementioned thermally induced carbon–carbon bond cleavage reactions was likely to be extremely difficult as the bonds formed to radical spin traps such as nitroxides are also expected to be labile at 300 °C.[45] Furthermore, the extreme conditions of thermal ROP precluded investigation into a radical mechanism by EPR spectroscopy. However, we anticipated that the proposed radicals were likely to participate in random radical coupling reactions with each other under thermolysis conditions to afford mixtures of cross-products. We, therefore, performed a series of co-thermolysis experiments to explore this possibility.

Our initial study involved a co-thermolysis of equimolar amounts of the dicarba[2]ferrocenophane *rac*-**14** and the ring-opened monomer **15** at 300 °C for 1 h. After work-up, two products were isolated, **17** (yield = 44 %) and **23** (yield = 32 %),[46] and their identities were confirmed by ^{1}H NMR and MS analysis (Scheme 14). High-resolution MS analysis of the residue (Figures S8–S12 in the Supporting Information) directly after the thermolysis showed, in addition to **17** and **23**, the presence of species **30**, **31** and **32**,[47] which were formed in yields too low to permit subsequent isolation (Figure 4).[48]



Scheme 14. Co-thermolysis of *rac*-**14** and **15 a** and **15 b** (only one isomer is shown).

For comparison, an analogous thermolysis of *rac*-**14** alone was performed at 300 °C for 1 h and the crude product was analysed by low-resolution MS. Interestingly no peaks were observed that could be assigned to the radical coupled product **32**, and *rac*-**14** was the sole species detected (Figure S6 in the Supporting Information). This result suggests that the proximity of the radical sites in short-lived intermediate **19** (Scheme 7), prohibits intermolecular coupling reactions in the absence of other radical species. However, contrasting reactivity was observed from the thermolysis of **15** alone (Scheme 9), where analysis of the crude product by low-resolution MS contained a peak at 550.1 *m/z* (10 %) assigned to species **30** (Figure S7 in the Supporting Information). Identification of **30** indicated that, in contrast to intermediate **19**, the lifetime of radical intermediate **21** may be sufficiently long to facilitate intermolecular coupling reactions to give a dimeric product.

Importantly, low-resolution MS analysis of the pure starting materials *rac*-**14** and **15** did not show any peaks associated with any higher molecular weight species. This allows the conclusion to be made that products **30**, **31** and **32** directly result from the thermolysis reactions and are not formed simply from *rac*-**14** and **15** during the analysis.

The reported observations allow conclusions to be made concerning the potential reactivity pathways of *rac*-**14** in the presence of an excess of the Cp anion at 300 °C (Scheme 7). Given the short life-time of intermediate **19**, as indicated in the previously reported isomerisation of *meso*/*rac*-**14** to *rac*-**14**,[49] and the result that this species does not undergo intermolecular radical coupling reactions with itself to give dimeric products, it is unlikely that the reaction of **19** with NaCp could occur sufficiently fast to facilitate complete conversion of *rac*-**14** to **17** in the 1 h reaction time.

Furthermore, the observation that ring-strain *is* a requirement for Fe–Cp bond cleavage in dicarba[2]ferrocenophanes indicates that the use of a large excess of Cp$^-$ could induce heterolytic cleavage of the Fe–Cp bond in *rac*-**14**, and that Fe–Cp bond cleavage is disfavoured following dicarba C–C bridge cleavage (mechanism A). From the thermal reactivity studies of species **15** and **16**, the dicarba spacer in the resulting intermediate (**18**) can be expected to undergo rapid homolytic cleavage under the thermolysis conditions employed, thus implicating mechanism B (Scheme 7).

Conclusion

New insight into the mechanistic processes that occur under the conditions of the thermal ROP of dicarba[2]ferrocenophanes has been revealed through studies of the thermal reactivity of *rac*-**14**, and also the corresponding ring-opened oligomers **15** and polyferrocenylethylene **16**. Our results indicated the presence of thermally induced homolytic cleavage of C–C bonds, with bulky Ph groups as substituents in the C$_2$ bridge or spacer, occurs selectively to afford the

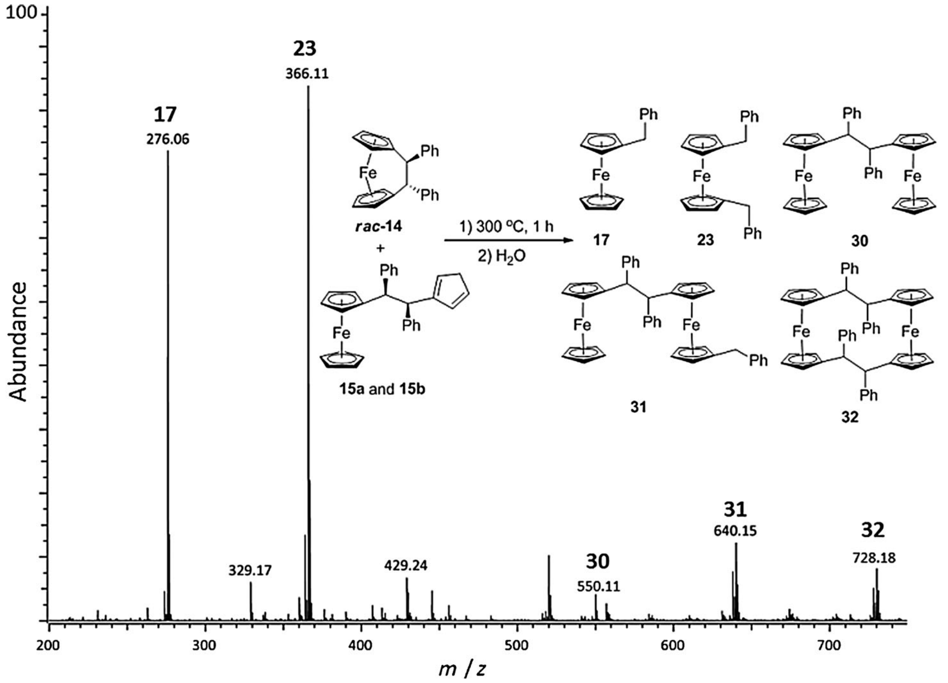


Figure 4. Low-resolution MS analysis of the co-thermolysis reaction of *rac*-**14** and **15**. Peak for **32** is overlapping with a peak at 730.1 *m/z* assigned to a linear dimer **35** (for details see Figure S10 in the Supporting Information).

acyclic ferrocene derivatives **17** or **23**. Comparison with the corresponding thermal behaviour of the linear trimer **29**, a species that lacks phenyl substituents and which is significantly more stable under identical reaction conditions, indicated that the presence of the bulky aryl substituents on adjacent carbons facilitates the selective C–C bond cleavage reactions.

Furthermore, the observation that these cleavage reactions occur for both the ring-opened species **15** and **16** as well as for the dicarba[2]ferrocenophane *rac*-**14** indicated that the presence of ring-strain is *not* a prerequisite for this type of process. Consistent with theory, the steric strain arising from the presence of the bulky Ph substituents on adjacent carbons presumably provides a key thermodynamic driving force for bond cleavage, and the resonance stabilisation of the radical intermediates thereby generated likely also plays an additional role.

Interestingly, the observation of higher molecular weight species, such as **30**, **31** and **32** from either the co-thermolysis of *rac*-**14** and **15** or the thermolysis of **15** alone, provided evidence for the coupling of radical intermediates formed from the thermally induced homolytic cleavage of the dicarba bridge or spacer. Further studies will aim to explore the role of analogous radical intermediates in the thermal reactivity of other [*n*]metallocenophanes.

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Keywords: carbon–carbon bond cleavage · dicarba[2]ferrocenophanes · radicals · ring-opening polymerization

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[21] A typical thermolysis experiment involved charging a Pyrex thermolysis tube with the reactants, evacuating the tube over 30 min, then sealing with an acetylene flame. The tube is then place in an oven for the duration of the thermolysis experiment. See the Experimental Section in the Supporting Information for further details.

[22] The moderate yield obtained for *rac*-**14** results from the formation of black material, postulated to be metallic Fe-based species, which absorbed to the chromatography column during purification, in addition to other products that could not be successfully separated and identified.

[23] L. Routaboul, J. Chiffre, G. G. A. Balavoine, J.-C. Daran, E. Manoury, *J. Organomet. Chem.* **2001**, *637–639*, 364–371.

[24] Excess magnesocene was quenched through the addition of H_2O, with extraction into DCM separating **17** from the by-products of the reaction.

[25] The intermediate in mechanism A, which can be described as a resonance hybrid of species **19** and **20**, has not been isolated, but is postulated to be generated in reactions of dicarba[2]ferrocenophanes involving homolytic cleavage of the dicarba bridge.

[26] Computational studies provided evidence for a contribution of the bisfulvenyl resonance form to the optimised structure of diradical intermediate **19**, predicting a C_{ipso}–C_{bridge} bond length between that of typical single and double C–C bonds.

[27] Several attempts to observe the fragmented species **22** by NMR spectroscopy were conducted, including cooling the thermolysis tube in liquid nitrogen prior to opening to trap any volatile species formed, however, none was successful.

[28] K. J. Stone, R. D. Little, *J. Org. Chem.* **1984**, *49*, 1849–1853.

[29] After heating at 300 °C for 1 h, although some signals corresponding to **22** were observed in ^{1}H NMR spectroscopic analysis of the crude product, the majority of the material consisted of a black solid, insoluble in common solvents which precluded spectroscopic analysis.

[30] Control experiments were conducted to assess the effect of Cp anion sources with both **15** and **17** at 300 °C for 1 h. In each case, the starting material was thermolysed with 5 equiv of $MgCp_2$. For **15**, identical reactivity was observed to that reported for the thermolysis of **15** alone, supporting the conclusion that **17** is formed through a radical mechanism. For **17**, no further reactivity was observed, allowing the conclusion to be made that ring-strain is a requirement for Fe–Cp bond cleavage reactions. For details see the Supporting Information.

[31] A peak at 4.14 ppm was observed in both the ^{1}H and ^{2}H NMR spectra and assigned to the η^5-C_5H_4D and/or η^5-C_5H_3RD groups through comparison with $[Fe(\eta^5\text{-}C_5H_4D)_2]$ (see the Supporting Information). This observation suggests that isotopic redistribution occurs in the melt, and indicates that initial deuterium incorporation into the product **17** maybe greater than 38 %.

[32] The isolated black material was not attracted to a bar magnet, suggesting no metallic iron-based species were present.

[33] The yield of **23** was calculated utilising the molecular weight of a single monomer unit of polyferrocenylethylene **16** to calculate the number of moles of polymer thermolysed (see the Supporting Information).

[34] S. Bhattacharyya, *J. Org. Chem.* **1998**, *63*, 7101–7102.

[35] MALDI-TOF analysis was conducted upon all materials in an attempt to observe the potential polymeric thermolysis products that occur upon carbon–carbon bond cleavage of the dicarba backbone. However, it was concluded that the MS data collected were not representative of the samples, as no peaks were observable above 4000 g mol^{-1}. Our findings are consistent with the literature (see ref. [17b]), where no MALDI-TOF MS data were reported.

[36] Further characterisation was conducted with **16c**. Analysis by UV/Vis spectroscopy was conducted and the spectra obtained did not display absorbances consistent with the presence of ferrocenyl units (λ_{max} = ca. 440 nm). Furthermore, ESI-MS was conducted and no signals corresponding to oligomeric species were observed. A small peak at 366.11 *m/z* was assigned to residual **23**. The characterisation conducted suggests that by-product **16c** is not low molecular weight polyferrocenylethylene but another paramagnetic by-product, perhaps formed from the thermal degradation of species **23**.

[37] E. Földes, G. Deak, F. Tüdös, O. Vogl, *Eur. Polym. J.* **1993**, *29*, 321–330.

[38] B. A. Howell, Y. Cui, D. B. Priddy, *Thermochim. Acta* **2003**, *396*, 167–177.

[39] Attempts to synthesise the diphenyl substituted trimer species by coupling of **15** were unsuccessful. Unreacted starting material was obtained in all cases.

[40] Thermolysis of **9** at 300 °C for 1 h resulted in further reactivity and decomposition. Upon purification multiple products were isolated, but due to the complexity of the ^{1}H NMR spectroscopic analysis, assignment of the chemical structure of each species could not be made (see the Supporting Information). No peaks were observed that could be assigned to the cyclopentadiene moiety in any of the isolated products, suggesting that this fragment is cleaved off during the thermolysis. The formation of multiple products is in contrast to the case of species **15a** and **15b**, in which selective labilisation of the central bond of the C–C spacer results in clean conversion to a new product (**17**) upon thermolysis.

[41] a) W. H. Morrison, Jr., S. Krogsrud, D. N. Hendrickson, *Inorg. Chem.* **1973**, *12*, 1998–2004; b) P. Aguirre-Etcheverry, D. O'Hare, *Chem. Rev.* **2010**, *110*, 4839–4864.

[42] A small amount (2 mg) of black material was isolated. The material was attracted to a bar magnet and was thus likely to contain metallic Fe.

[43] Thermolysis of trimer **29** at 300 °C for 16 h resulted in thermal decomposition with a negligible amount of trimer **29** and mainly other unidentified products isolated.

[44] The weakening of the C–C bond in dicarba[2]ferrocenophanes through the introduction of bulky substituents has been experimentally observed through X-ray crystallographic analysis, in which the dicarba bridge bond length increases from 1.545(3) Å in species bearing all hydrogen substituents, to 1.612(3) Å in a dicarba[2]ferrocenophane bearing one bulky *t*Bu substituents on each carbon of the dicarba bridge (see ref. [20] for details).

[45] The thermal stability of common radical traps was investigated in order to explore whether the radical mechanism proposed could be verified through trapping of the intermediates. However, control thermolysis experiments under our standard experimental conditions (300 °C, 1 h) for both TEMPO and the galvinoxyl radical resulted in thermal decomposition. Thermolysis of **15a/b** in the presence of an excess of thermally stable trityl deuteride (Ph_3CD) did not result in any deuterium incorporation in **17**, perhaps due to the steric restrictions of the trityl species.

[46] The yields for **17** and **23** are based on the amount of **15** and *rac*-**14** thermolysed, respectively. Due to the inability to completely separate species **17** and **23** by column chromatography, yields were calculated through integration of characteristic signals in the ^{1}H NMR spectra. For details see the Supporting Information.

[47] Additional high molecular weight peaks were observed in the low-resolution mass spectrometric analysis. These species could not be assigned to logical products from the coupling of radical intermediates, and are most likely fragments of the higher molecular weight oligomeric species that result through coupling.

[48] Due to overlapping signals in the ^{1}H NMR spectrum, the radically coupled species could not be identified. Attempted isolation using column chromatography was unsuccessful. Their presence was identified, however, through high-resolution mass spectrometric analysis. The above observations suggested that these species were formed in very low yield.

[49] Cleavage of the dicarba bridge in species *rac*-**14** is likely to occur rapidly, however, the rate of isomerisation of *meso/rac*-**14** to *rac*-**14** is relatively slow (300 °C, 16 h; see ref. [19] for details). This suggests that although the equilibration between *meso*/*rac*-**14** and diradical intermediate **19** at thermolysis temperatures (300 °C) is rapid, the short lifetime of intermediate **19** disfavours Cp_{ispo}–C_{bridge} bond rotation, which must occur to facilitate isomerisation, as the time required for this operation is significantly longer.

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