



## Preparation and some chemistry of ferrocenylethynyl ketones

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### ARTICLE INFO

#### Article history:

Received 18 August 2009

Received in revised form 19 October 2009

Accepted 20 October 2009

Available online 24 October 2009

#### Keywords:

Ferrocene

Alkyne

Ketone

Vinylidene

### ABSTRACT

Reactions of  $\text{Fc}'(\text{CHO})_2$  **1** ( $\text{Fc}' = 1,1'$ -ferrocenediyl) with  $\text{LiC}\equiv\text{CR}$  gave substituted propargylic alcohols  $\text{Fc}'\{\text{CH}(\text{OH})\text{C}\equiv\text{CR}\}_2$  ( $\text{R} = \text{SiMe}_3$  **2**,  $\text{Fc}$  **9**). Oxidation ( $\text{MnO}_2$ ) of these alcohols afforded the bis(alkynyl ketone)s  $\text{Fc}'\{\text{C}(\text{O})\text{C}\equiv\text{CR}\}_2$  ( $\text{R} = \text{SiMe}_3$  **3**,  $\text{Fc}$  **10**), the former being accompanied by the partially desilylated  $\text{Fc}'\{\text{C}(\text{O})\text{C}\equiv\text{CH}\}-1-\{\text{C}(\text{O})\text{C}\equiv\text{CSiMe}_3\}-1'$  **4**. The reaction between **4** and  $\text{RuCl}(\text{dppe})\text{Cp}$  in the presence of  $\text{Na}[\text{BPh}_4]$  gave the cyclic vinylidene complex  $[\text{Ru}\{\text{C}\equiv\text{C}[\text{C}(\text{O})\text{Fc}'\text{C}(\text{O})\text{CH}=\text{CH}]\}(\text{dppe})\text{Cp}]\text{BPh}_4$  **5**. The diastereomers were separated by flash chromatography (**2**) or preparative t.l.c. (**9**) to give the *cis* (**2a**, **9a**) and *trans* (**2b**, **9b**) isomers. Cyclisation of each isomer to the corresponding ferrocenophane was catalysed by pTSA to give  $\text{Fc}'\{\text{CH}(\text{C}\equiv\text{CR})\}_2\text{O}$  ( $\text{R} = \text{SiMe}_3$  **6a**, **6b**;  $\text{Fc}$  **11a**, **11b**), of which **6a**, **6b** could be desilylated to  $\text{Fc}'\{\text{CH}(\text{C}\equiv\text{CH})\}_2\text{O}$  **7a**, **7b**, and further transformed into the bis( $\eta^2$ -alkyne-dicobalt) complexes  $\text{Fc}'\{\text{CH}(\eta^2\text{-C}_2\text{H}[\text{Co}_2(\mu\text{-dppm})(\text{CO})_4])\}_2\text{O}$  **8a**, **8b** with  $\text{Co}_2(\mu\text{-dppm})(\text{CO})_6$ . Molecular structures of **3**, **5**, **6a**, **6b**, **7a**, **7b** and **10** were determined by single-crystal XRD methods.

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### 1. Introduction

Mono- and bis-alkynyl ketones are useful precursors, particularly in recent studies of carbon-rich compounds and conjugated organic scaffolds [1]. The carbonyl group can be more or less readily converted to  $\text{C}=\text{CX}_2$  ( $\text{X} = \text{H}, \text{Br}, \text{CN}$ ) groups, some of which can be treated, e.g., in Sonogashira reactions, to introduce further unsaturation. We have begun a study of compounds of this type which also bear organometallic end-groups, some of which are redox-active. The initial aim of this chemistry was to find a convenient route to bis-butadiynes using Corey–Fuchs reactions from the bis-vinyl bromide [2]. Applications of this reaction to the syntheses of bis(ferrocenyl)-substituted 1,4-di- and 1,1,4,4-tetraethynylbutatrienes [3] and to 1,6-bis(ferrocenyl)hexatriyne [4] have been described. The close proximity of the two functional groups ( $\text{C}\equiv\text{C}$  and  $\text{C}=\text{O}$ ), the former of which can be modified by electron-rich transition metal moieties, such as  $\text{Ru}(\text{dppe})\text{Cp}$ , also offers the opportunity of enhancing the subsequent reactivity of these compounds.

This paper describes some results obtained during a study of alkynyl ketones which contain 1,1'-ferrocenediyl ( $\text{Fc}'$ ) groups. In principle, these derivatives should be redox active, while the electron-donating metallocene should modify their subsequent chemistry. The simplest compound,  $\text{FcC}(\text{O})\text{C}\equiv\text{CH}$ , has been described on several previous occasions, initially being obtained by Schlögl [5], and later by Akiyama et al. [6], with more efficient syntheses being

reported more recently by Torroba et al. [7] and by fluoride-induced desilylation of  $\text{FcC}(\text{O})\text{C}\equiv\text{CSiMe}_3$  [8]. Related alkynyl ketones have been converted to longer poly-yne via the dibromomethylene derivative [9]. Incorporation into self-assembled monolayers by “click” reactions with azides enables quantification of the redox centres on surfaces [10,11].

However, 1,1'-disubstituted ferrocenes containing two alkynyl-carbonyl groups are apparently unknown, there being no reports of the molecules  $\text{Fc}'\{\text{C}(\text{O})\text{C}\equiv\text{CR}\}_2$  ( $\text{R} = \text{H}, \text{SiMe}_3$ ), for example. This paper describes the syntheses of these compounds, together with a preliminary study of their chemistry. They have been used to make a range of ferrocenophanes bearing alkynyl groups, which have been subsequently converted to characteristic dicobalt carbonyl or ruthenium vinylidene complexes. Some related chemistry of compounds containing three ferrocene nuclei is also described.

### 2. Results and Discussion

The chemistry described below is summarised in Schemes 1 and 2. The various complexes have all been characterised by microanalysis and from their spectral properties (Table 1). Most  $^{13}\text{C}$  NMR resonances have been assigned using 2D HMBC and HMQC experiments. In selected cases, single-crystal XRD structural studies have confirmed the molecular structures.

Reactions of ferrocene-1,1'-dialdehyde  $\text{Fc}'(\text{CHO})_2$  **1** [ $\text{Fc}' = \text{ferrocene-1,1'-diyl}$ ,  $\text{Fe}(\eta\text{-C}_5\text{H}_4\text{-})_2$ ] with alkynyllithium reagents  $\text{LiC}\equiv\text{CR}$  ( $\text{R} = \text{SiMe}_3, \text{Fc}$ ) at  $-78^\circ\text{C}$  have given the corresponding propargylic alcohols  $\text{Fc}'\{\text{CH}(\text{OH})\text{C}\equiv\text{CR}\}_2$  which form yellow to orange oils ( $\text{R} = \text{SiMe}_3$  **2**) or solids ( $\text{R} = \text{Fc}$  **9**). The diastereomers of each of these

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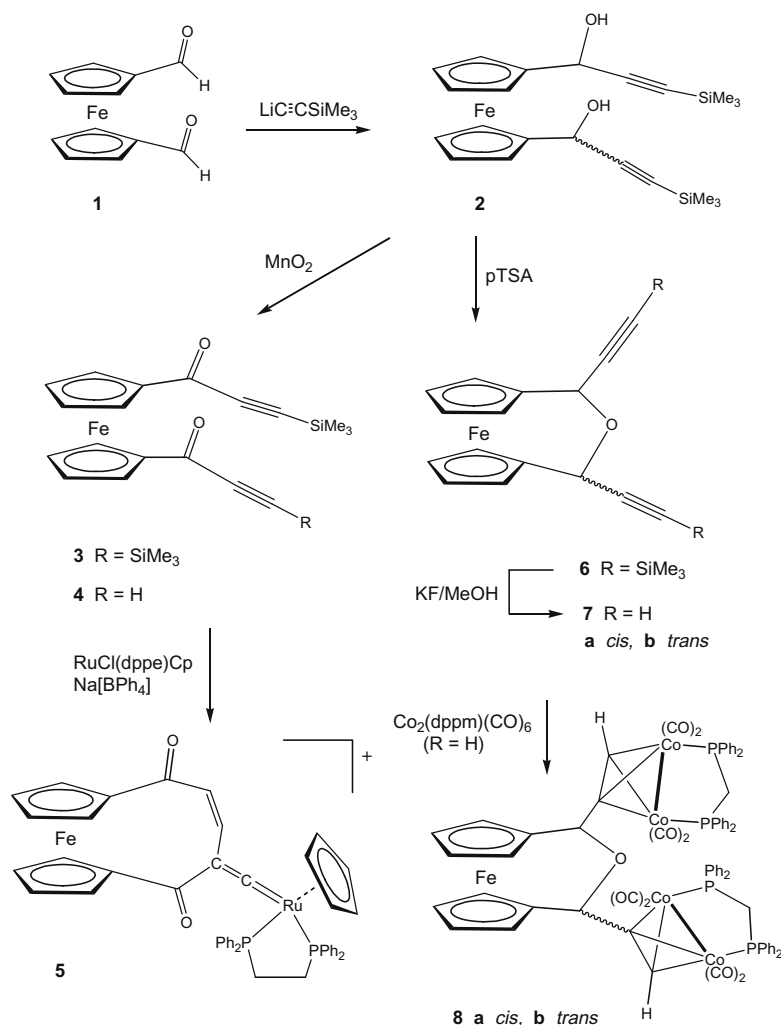
**Table 1**  
Selected bond parameters for ferrocenylalkynyl ketones **3** and **10**<sup>a</sup>.

| Compounds                 | <b>3</b>           | <b>10</b> <sup>a</sup>                             |
|---------------------------|--------------------|--|
| <i>Bond distances (Å)</i> |                    |  |
| Fe–C(cp)                  | 2.027–<br>2.061(2) | 2.039–2.053(5); 2.031–2.060(5); 2.037–<br>2.049(5) |
| (av.)                     | 2.044              | 2.045; 2.042; 2.044                                |
| Fe(1)–C(101)              | 2.032(2)           | 2.039(5)   |
| Fe(2)–C(201)              |                    | 2.040(4)   |
| Fe(3)–C(301)              |                    |  |
| C(1)–O(1)                 | 1.227(3)           | 1.25(2)  |
| C(1)–C(2)                 | 1.459(4)           | 1.46(2)  |
| C(1)–C(101)               | 1.453(3)           | 1.47(2)  |
| C(2)–C(3)                 | 1.198(4)           | 1.21(1)  |
| C(3)–C(201)               |                    | 1.413(9)   |
| C(3)–Si                   | 1.849(3)           |  |
| <i>Bond angles (°)</i>    |                    |  |
| C(2)–C(1)–O(1)            | 120.8(2)           | 118.7(17)  |
| C(101)–C(1)–O(1)          | 123.0(2)           | 119.4(13)  |
| C(101)–C(1)–C(2)          | 116.2(2)           | 122.0(11)  |
| C(1)–C(2)–C(3)            | 178.3(3)           | 178.6(11)  |
| C(2)–C(3)–X               | 178.0(2) [Si]      | 177.5(8) [C(201)]                                  |

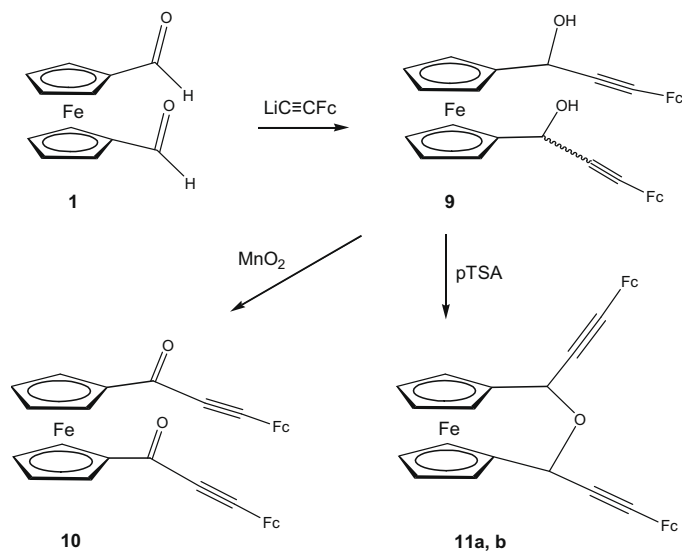
<sup>a</sup> C(4)–O(4) 1.18(3), C(4)–C(5) 1.45(2), C(5)–C(6) 1.20(2) Å; C(4)–C(5)–C(6) 175.9(15), C(5)–C(6)–C(301) 175.7(12), C(101)–C(4)–O(4) 116.1(15), C(101)–C(4)–C(5) 119.7(19)°.

compounds can be separated by column chromatography on silica gel. The diastereomeric mixture of **2** was oxidised with MnO<sub>2</sub> to give a mixture of Fc{C(O)C≡SiMe<sub>3</sub>}<sub>2</sub> **3** and the partially desilylated compound Fc'-1-{C(O)C≡SiMe<sub>3</sub>}-1'-{C(O)C≡CH} **4**, obtained in 57% and 15% yields, respectively, as dark red solids. Formation of the latter may result from weakening of the Si–C bond by conjugation with the electron-withdrawing carbonyl function. The triferrocene **9** is similarly oxidised to Fc{C(O)C≡CFc}<sub>2</sub> **10** which forms dark red crystals. To our knowledge, these compounds are the first examples of 1,1'-bis(alkynylcarbonyl)ferrocenes.

The unusual cyclic vinylidene [5]BPh<sub>4</sub> was obtained from the reaction between Fc'-1-{C(O)C≡SiMe<sub>3</sub>}-1'-{C(O)C≡CH} **4** and RuCl(dppe)Cp in the presence of Na[BPh<sub>4</sub>]. The structure of this complex was determined from a single-crystal XRD study, crystals of the 1.75CHCl<sub>3</sub> solvate being obtained from chloroform. Spectroscopic properties are in accord with the solid state structure, particularly the down-field resonance for the Ru=C atom at δ<sub>C</sub> 345.7; the two C=O resonances are at δ<sub>C</sub> 184.06 and 195.55. In this reaction, cyclisation occurs by attack of the ruthenium centre at the ethynyl group to give the corresponding vinylidene, which after deprotonation, undergoes intramolecular Michael addition/cyclisation with the α,β-unsaturated alkynylketone on the other C<sub>5</sub> ring to form the cyclic vinylidene (Scheme 3). Desilylation, which occurs at neutral pH and in the absence of fluoride, may also take place during the formation of the initial vinylidene.



**Scheme 1.**



Scheme 2.

Following earlier studies [12], treatment of the propargylic alcohols **2** and **9** with a catalytic amount of 4-toluenesulfonic acid (pTSA) in refluxing benzene resulted in ring closure to afford the corresponding bis(alkynyl)-[3]-ferrocenophanes  $\text{Fc}\{[\text{CH}(\text{C}\equiv\text{CR})_2\text{O}]\}_2$  ( $\text{R} = \text{SiMe}_3$  **6**,  $\text{Fc}$  **11**). For  $\text{R} = \text{SiMe}_3$ , flash chromatography (silica gel) separated the *cis* (**6a**; 29%) and *trans* (**6b**; 44%) isomers as light yellow solids, the latter being the slower moving. The structures of both isomers were confirmed by single-crystal XRD studies. Subsequent desilylation of the pure isomers with KF in MeOH/thf afforded the ethynyl compounds  $\text{Fc}\{[\text{CH}(\text{C}\equiv\text{CH})_2\text{O}]\}_2$  **7a** and **7b** in essentially quantitative yields. The bis(ferrocenylalkynyl)-[3]-ferrocenophane **11** was separated by preparative t.l.c. to give the *cis* (**11a**; 13%) and *trans* (**11b**; 72%) isomers as yellow solids. The latter is the slower moving and could be subsequently crystallised from toluene.

Reactions of the bis(ferrocenylethynyl)-[3]-ferrocenophanes **7a** and **7b** with  $\text{Co}_2(\mu\text{-dppm})(\text{CO})_6$  afforded the corresponding bis( $\eta^2$ -alkyne-dicobalt) complexes **8a** and **8b** as maroon solids (28% and

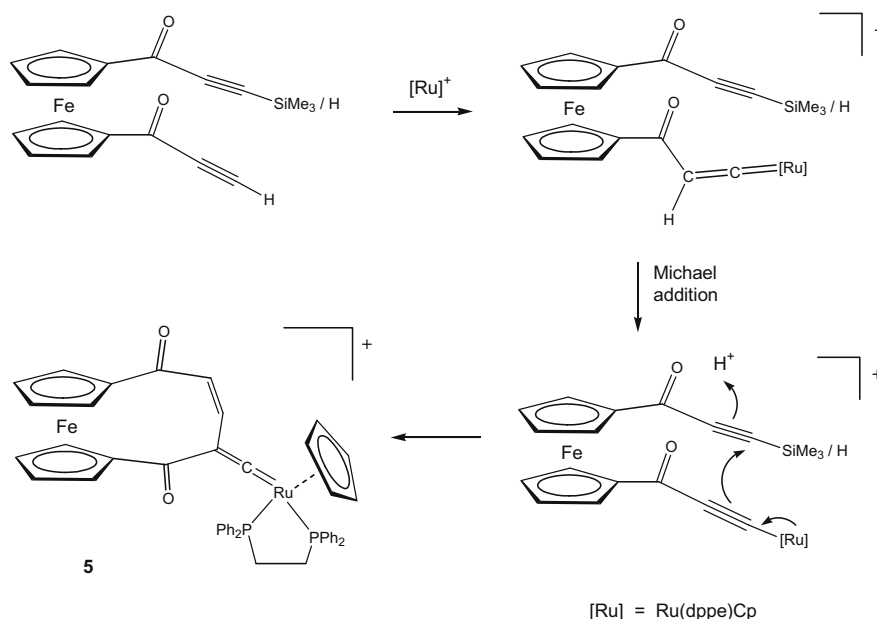
53% yields, respectively). These complexes were unstable and did not survive attempted purification by chromatography on the usual adsorbents. Instead, both compounds were purified by crystallisation ( $\text{Et}_2\text{O}/\text{hexane}$ ) and characterised by microanalysis and from their spectroscopic properties.

## 2.1. Molecular structures

Plots of single molecules of complexes **3**, **6a**, **6b**, **7a**, **7b** and **10** are shown in Figs. 1–4, selected bond parameters being collected in Tables 1 and 2. Overall, the latter are in accord with those found for many ferrocenes with related substituents and do not merit detailed discussion. In **6** and **7**, the shortest Fe–C(cp) separations are to C(201), the ring carbon that bears the substituent, with values of between 1.992(2) and 2.003(2) Å. In the [3]-ferrocenophanes, the three-atom link between the  $\text{C}_5$  rings results in close to eclipsed conformations for the  $\text{C}_5$  rings ( $\theta$  between  $0.3^\circ$  and  $6.7^\circ$ ) and the  $\text{Cp}^0\text{-Fe-Cp}^0$  angles ( $\text{Cp}^0 = \text{centroids of Cp rings}$ ) deviate somewhat from linearity ( $171.9\text{--}172.4^\circ$ ). The dimensions of the  $-\text{C}(\text{O})\text{-C}\equiv\text{C}-$  fragments show little or no effect of the juxtaposition of the two groups on their individual bond lengths/angles, with  $\text{C}=\text{O}$  between 1.227(3) and 1.25(2) Å and  $\text{C}\equiv\text{C}$  between 1.198(4) and 1.227(3) Å.

The molecule of **3** (Fig. 1) contains a transoid arrangement of the alkynylcarbonyl substituents, resulting in staggered  $\text{C}_5$  rings ( $\theta = 36^\circ$ ) (Fig. 1). The crystal of **10** contains two chiral planar isomers (Fig. 2), the carbonyl groups being in a cisoid arrangement, resulting in almost eclipsed  $\text{C}_5$  rings in the central ferrocene ( $\theta = 2.1^\circ$ ). There is no obvious reason for the partial resolution in the crystal: in solution, the NMR spectra indicate a low barrier for rotation, so that it is the thermodynamic isomer which is obtained.

The  $\text{Ru}(\text{dppe})\text{Cp}$  fragment in the cation of **[5]BPh<sub>4</sub>** (Fig. 5, Table 3) has the common pseudo-octahedral geometry, with  $\text{Ru-P}(1,2)$  2.2970, 2.2988(2) and  $\text{Ru-C}(\text{cp})$  2.256–2.280(1) Å; angles  $\text{P}(1)\text{-Ru-P}(2)$  and  $\text{P}(1,2)\text{-Ru-C}(1)$  are  $82.26(1)^\circ$ ,  $82.93(2)^\circ$  and  $91.34(3)^\circ$ , respectively. The  $\text{Ru}=\text{C}(1)=\text{C}(2)\text{-C}(3,6)$  unit has  $\text{Ru-C}(1)$  1.845(1),  $\text{C}(1)\text{-C}(2)$  1.321(1) and  $\text{C}(2)\text{-C}(3,6)$  separations of 1.476(1), 1.526(1) Å, with angles  $\text{Ru-C}(1)\text{-C}(2)$   $175.93(7)^\circ$  and  $\text{C}(1)\text{-C}(2)\text{-C}(3,6)$   $119.78(9)^\circ$ ,  $118.02(8)^\circ$ , respectively. The two immediate substituents of  $\text{C}_\beta$  are the carbonyl group  $\text{CO}(6)$  [ $\text{C}=\text{O}$  1.220(1) Å] and



Scheme 3.

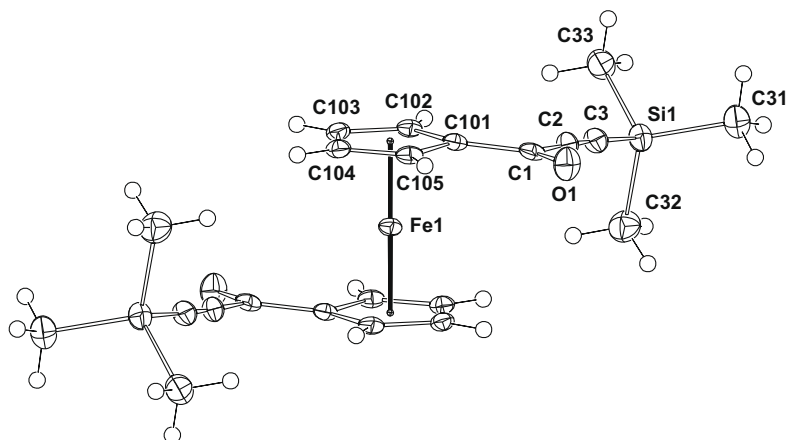


Fig. 1. Plot of a molecule of  $\text{Fc}\{\text{C}(\text{O})\text{C}=\text{CSiMe}_3\}_2$  **3**.

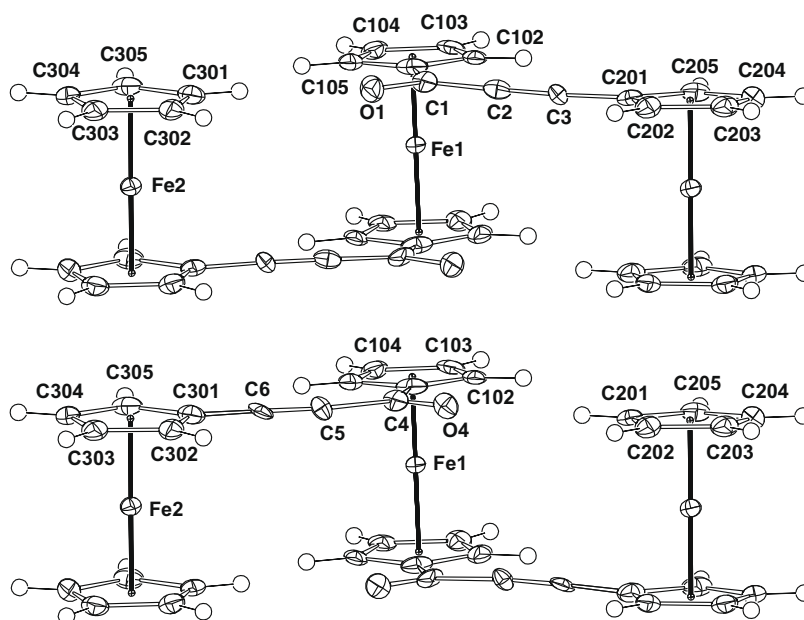


Fig. 2. Plots of molecules of the major (upper) and minor (lower) components of  $\text{Fc}\{\text{C}(\text{O})\text{C}=\text{CFc}\}_2$  **10**.

the vinyl group  $\text{C}(3)=\text{C}(4)$  [1.335(2) Å], which have the normal geometries. This complex can also be considered as a novel example of a [5]-ferrocenophane, the  $\text{C}_5$  bridge between the two rings having little effect on the  $\text{Cp}^0\text{-Fe-Cp}^0$  angle ( $178.8^\circ$ ), in contrast with the [3]-ferrocenophanes mentioned above.

## 2.2. Redox data

The Fc nuclei are redox active and we have measured the CVs of most compounds isolated during this work (Table 4). Only a single 1-e oxidation process is found for **2**, **6** and **7**, within the range +0.54 to +0.70 V, reflecting the differing electron-withdrawing character of the various substituents. For **9**, all three Fc centres have similar potentials, not resolved in the CV. In all cases, oxidation potentials are greater than that of ferrocene itself as a result of decreasing electron density at the ferrocene nucleus.

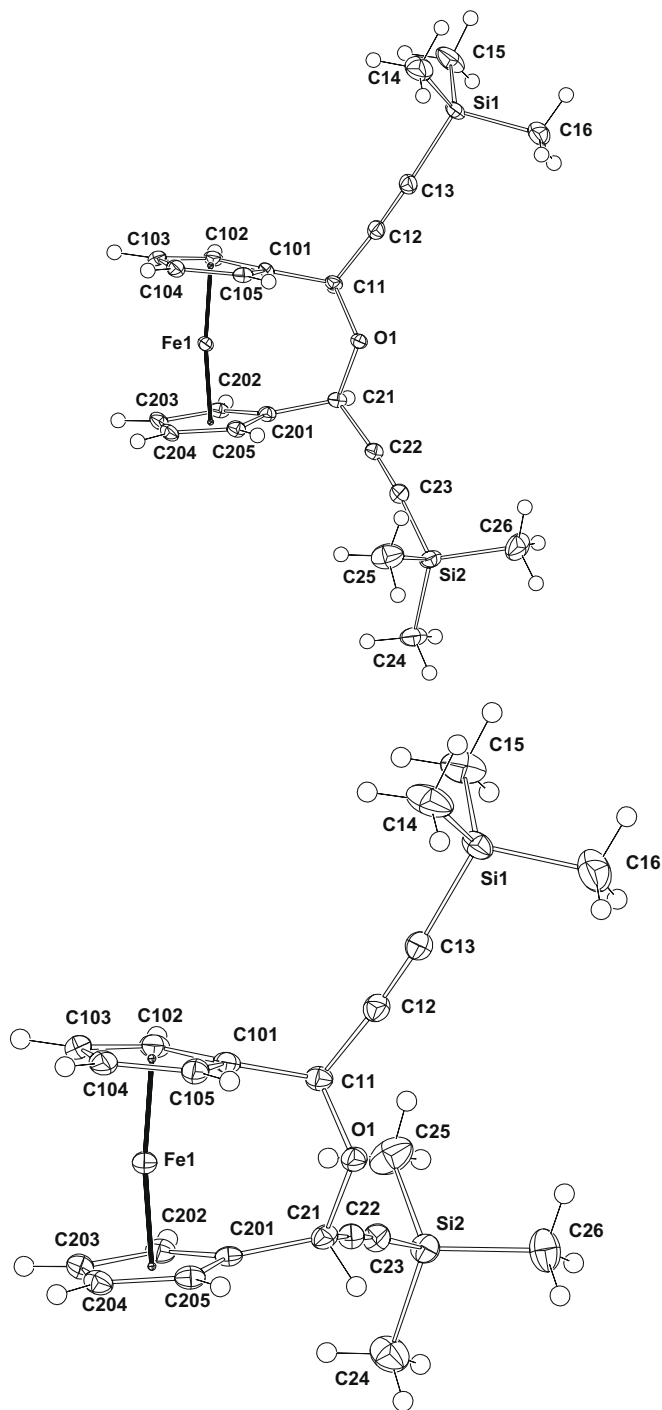
Vinylidene **5** shows two oxidation waves, which are likely to be at the ruthenium (+0.88 V, irreversible) and ferrocene (+0.92 V, reversible) centres, respectively. In the cases of **3–5**, 1-e reduction waves at ca –1.45 V suggest that reduction at the carbonyl groups can occur readily. The dicobalt complexes exhibit several oxidation

steps, two of which at ca +0.40, +0.74 V are likely to be centre on the  $\text{C}_2\text{Co}_2$  fragment.

Compounds containing three Fc nuclei give either one or two oxidation waves between +0.54 and +0.70 V. For **10**, the two alkynylferrocene moieties are oxidised at +0.70 V, while the presence of the carbonyl groups makes the central Fc nucleus harder to oxidise (a 1-e process at +1.11 V), while for **11a** (*cis*), a 2-e process at +0.56 V is followed by a 1-e process at +0.65 V, suggesting that the two alkynylferrocene moieties are oxidised at the lower potential, as expected for the electron-rich  $\text{Fc}\equiv\text{C}$  substituent. For the *trans* isomer (**11b**), only one 3-e process is observed at +0.54 V.

## 3. Conclusions

This paper describes the first syntheses and characterisation of 1,1'-bis(alkynylcarbonyl)ferrocenes, together with their reduction to propargylic alcohols and the cyclisation of some of these to the corresponding [3]-ferrocenophanes. The ethynyl groups in **7a**, **7b** readily bond to  $\text{Co}_2(\mu\text{-dppm})(\text{CO})_4$  fragments to give complexes of limited stability, while the mixed proto-/trimethylsilyl-ethynyl dicarbonyl derivative **4** undergoes a novel reaction upon treatment



**Fig. 3.** Plots of molecules of [3]-ferrocenophanes *cis*-Fc'[[CH(C≡CSiMe<sub>3</sub>)<sub>2</sub>O] **6a** (upper) and *trans*-Fc'[[CH(C≡CSiMe<sub>3</sub>)<sub>2</sub>O] **6b** (lower).

with RuCl(dppe)Cp to give the cyclic vinylidene complex **5**. Complexes containing ferrocenylethynylcarbonyl groups and the derived propargylic alcohols and cyclophanes represent the first examples of their type containing three ferrocene nuclei.

## 4. Experimental

### 4.1. General

All reactions were carried out under dry nitrogen, although normally no special precautions to exclude air were taken during

subsequent work-up. Common solvents were dried, distilled under nitrogen and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates (20 × 20 cm<sup>2</sup>) coated with silica gel (Merck, 0.5 mm thick).

### 4.2. Instruments

IR spectra: Bruker IFS28 FT-IR spectrometer. Spectra in CH<sub>2</sub>Cl<sub>2</sub> were obtained using a 0.5 mm path-length solution cell with NaCl windows. Spectra of Nujol mulls or of thin films were obtained from samples mounted between NaCl discs. NMR spectra: Varian 2000 (<sup>1</sup>H at 300.13 MHz, <sup>13</sup>C at 75.47 MHz, <sup>31</sup>P at 121.503 MHz). Unless otherwise stated, samples were dissolved in CDCl<sub>3</sub> contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for <sup>1</sup>H and <sup>13</sup>C NMR spectra and external H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P NMR spectra. Electrospray mass spectra (ES-MS, positive ion mode): Fisons VG Platform II spectrometer. Solutions in MeOH (unless otherwise indicated) were injected into a via a 10 ml injection loop; NaOMe was added as an aid to ionisation [13]. Nitrogen was used as the drying and nebulising gas. Ions listed are the most intense in the respective ion clusters. CVs were recorded from solutions in CH<sub>2</sub>Cl<sub>2</sub> ca 10<sup>-4</sup> M in analyte also containing 10<sup>-1</sup> M [NBu<sub>4</sub>]BF<sub>4</sub> in a single-compartment three-electrode cell equipped with platinum working, coiled platinum wire auxiliary and platinum wire pseudo-reference electrodes at scan rates of 50–800 mV s<sup>-1</sup>. All redox potentials are reported vs. SCE, with the FeCp<sub>2</sub>/[FeCp<sub>2</sub>]<sup>+</sup> redox couple (+0.46 V vs. SCE) used as internal reference. Elemental analyses were by Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

### 4.3. Reagents

The compounds RuCl(dppe)Cp [14], 1,1'-Fc'(CHO)<sub>2</sub> [15] and FcC≡CH [16] were obtained as previously described.

### 4.4. Trimethylsilyl ethynyl derivatives

#### 4.4.1. 1,1'-Fc' {CH(OH)C≡CSiMe<sub>3</sub> }<sub>2</sub> **2**

To a solution of HC≡CSiMe<sub>3</sub> (823 mg, 8.38 mmol) in dry thf (50 mL) at -78 °C was added *n*-BuLi (5.0 mL, 1.6 M in hexanes, 8.0 mmol) and the resulting mixture was stirred for 30 min. 1,1'-Fc'(CHO)<sub>2</sub> (500 mg, 2.07 mmol) was then added and the solution allowed to warm until all the solids had dissolved. After cooling again to -78 °C and stirring for a further 30 min, the mixture was quenched by addition of saturated aqueous NH<sub>4</sub>Cl. The crude biphasic mixture was extracted twice with Et<sub>2</sub>O and the combined organic fractions were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and the solvent removed under vacuum. The crude residue was purified by column chromatography (silica gel, Et<sub>2</sub>O-hexane, 2/3) to afford separate diastereomers of 1,1'-Fc' {CH(OH)C≡CSiMe<sub>3</sub> }<sub>2</sub> **2a, b**.

Isomer **2a** (*R*<sub>f</sub> = 0.32) formed an orange oil (336 mg, 37%). IR (neat)/cm<sup>-1</sup>: ν(OH) 3293s, ν(C≡C) 2175 m, 2176 m. <sup>1</sup>H NMR: δ 0.25 (s, 18H, SiMe<sub>3</sub>), 3.70 (d, *J* = 6.3 Hz, 2H, CHOH), 4.20–4.25, 4.33–4.35, 4.48–4.49 (3 × m, 4 + 2 + 2H, FeC<sub>5</sub>H<sub>4</sub>), 5.25 (d, *J* = 6.3 Hz, 2H, CHOH). <sup>13</sup>C NMR: δ -0.08 (SiMe<sub>3</sub>), 60.73 (CHOH), 67.41, 68.15, 68.76, 68.90, 89.07 (C≡C), 90.03 (*ipso* of FeC<sub>5</sub>H<sub>4</sub>), 105.68 (C≡C). ES-MS (*m/z*): 461, [M+Na]<sup>+</sup>; 438, M<sup>+</sup>; 421, [M-OH]<sup>+</sup>. HR-MS (C<sub>22</sub>H<sub>30</sub>FeO<sub>2</sub>Si<sub>2</sub>): calcd 438.1134, found 438.1197.

Isomer **2b** (*R*<sub>f</sub> = 0.25) was an orange oil (504 mg, 55%). IR (neat)/cm<sup>-1</sup>: ν(OH) 3306s, ν(C≡C) 2174 m. <sup>1</sup>H NMR: δ 0.24 (s, 18H, SiMe<sub>3</sub>), 3.12 (d, *J* = 7.2 Hz, 2H, CHOH), 4.22–4.24, (m, 4H, FeC<sub>5</sub>H<sub>4</sub>), 4.37 (d, *J* = 1.5 Hz, 2H, FeC<sub>5</sub>H<sub>4</sub>), 4.42 (d, *J* = 1.5 Hz, 2H, FeC<sub>5</sub>H<sub>4</sub>), 5.21 (d, *J* = 7.2 Hz, 2H, CHOH). <sup>13</sup>C NMR: δ -0.10 (SiMe<sub>3</sub>), 61.00 (CHOH), 67.13, 68.61, 68.93, 69.13, 89.31 (C≡C), 89.91 (*ipso* of FeC<sub>5</sub>H<sub>4</sub>), 105.49 (C≡C). ES-MS (*m/z*): 461, [M+Na]<sup>+</sup>; 438, M<sup>+</sup>; 421,

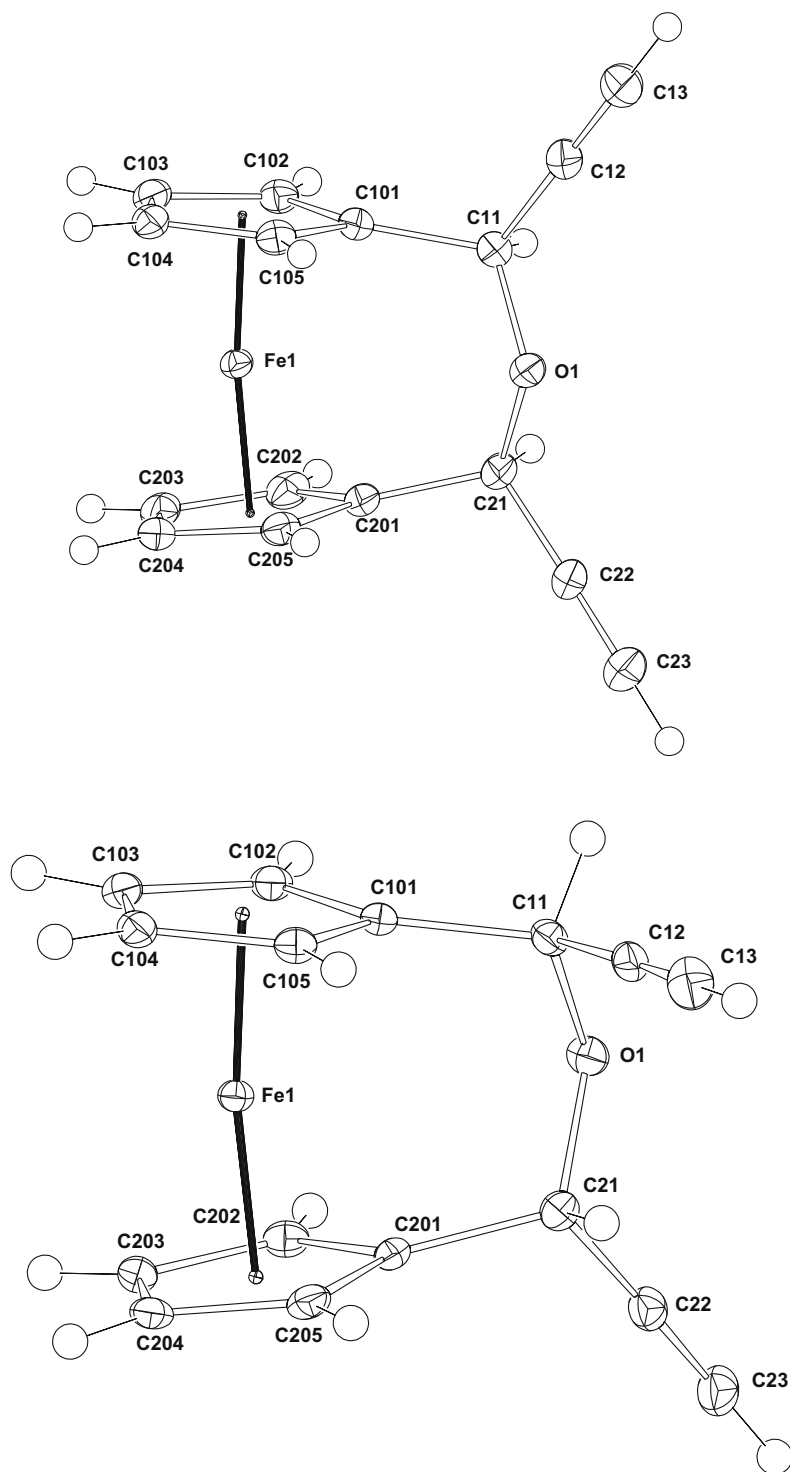


Fig. 4. Plots of molecules of [3]-ferrocenophanes *cis*-Fc'([CH(C=CH)]<sub>2</sub>O) **7a** (upper) and *trans*-Fc'([CH(C=CH)]<sub>2</sub>O) **7b** (lower).

[M–OH]<sup>+</sup>. HR-MS: calcd (C<sub>22</sub>H<sub>30</sub>FeO<sub>2</sub>Si<sub>2</sub>) 438.1134, found 438.1188.

#### 4.4.2. 1,1'-Fc' {C(O)C≡CSiMe<sub>3</sub>}<sub>2</sub> **3** and Fc' {C(O)C≡CSiMe<sub>3</sub>} {C(O)C≡CH} **4**

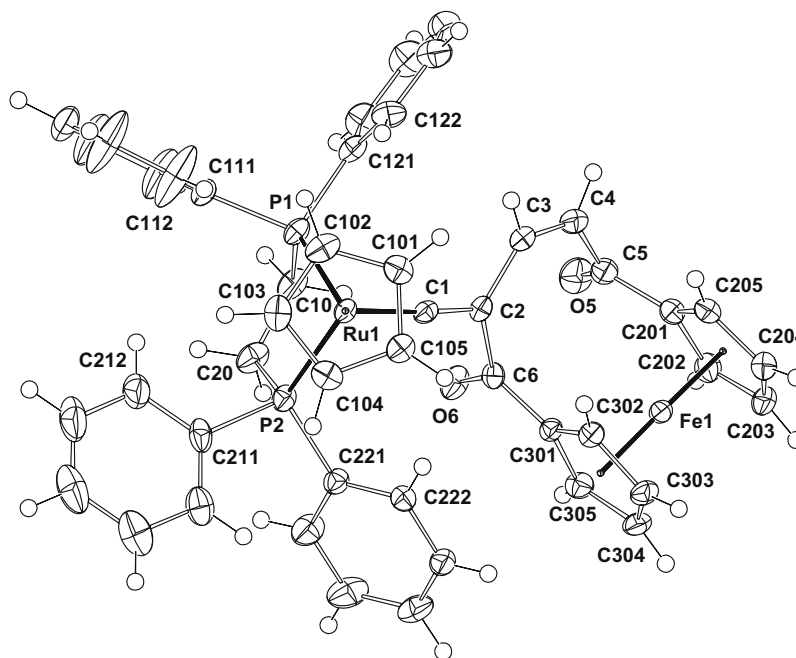
MnO<sub>2</sub> (7.5 g) was added to a rapidly stirred solution of 1,1'-Fc' {CH(OH)C≡CSiMe<sub>3</sub>}<sub>2</sub> (830 mg, 1.90 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and the resulting suspension was stirred vigorously for 30 min. The mixture was passed through a short pad of celite and the solvent reduced to a few mL. The solution was subjected to flash col-

umn chromatography (silica gel, EtOAc-hexane, 1/4) to afford the following products:

1,1'-Fc' {C(O)C≡CSiMe<sub>3</sub>}<sub>2</sub> **3**: (R<sub>f</sub> = 0.47), dark red solid (465 mg, 57%), crystallised from CH<sub>2</sub>Cl<sub>2</sub>/MeOH. Anal. Calc. for C<sub>22</sub>H<sub>26</sub>FeO<sub>2</sub>Si<sub>2</sub>: C, 60.82; H, 6.03; M, 434. Found: C, 61.08; H, 6.11%. IR (nujol)/cm<sup>-1</sup>: ν(C≡C) 2152w, ν(C=O) 1623s, ν(C=C) 1588 m. <sup>1</sup>H NMR: δ 0.34 (s, 18H, SiMe<sub>3</sub>), 4.64 (s, 4H, C<sub>5</sub>H<sub>4</sub> of Fc), 4.98 (s, 4H, C<sub>5</sub>H<sub>4</sub> of Fc). <sup>13</sup>C NMR: δ -0.59 (SiMe<sub>3</sub>), 72.19, 72.31, 75.55, 75.63, 81.40 (*ipso* of Fc), 97.88 (C≡C), 101.42 (C=C), 179.79 (C=O). ES-MS (*m/z*): 457, [M+Na]<sup>+</sup>. X-ray quality crystals were grown from dichloromethane/hexane.

**Table 2**  
Selected bond parameters for [3]-ferrocenophanes **6a**, **6b**, **7a** and **7b**.

| Compounds                           | <b>6a</b>                      | <b>6b</b>                      | <b>7a</b>                      | <b>7b</b>                      |
|-------------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| <i>Bond distances (Å)</i>           |                                |                                |                                |                                |
| Fe–C(cp)                            | 1.992–2.082(2); 2.003–2.064(2) | 1.994–2.052(2); 2.002–2.054(2) | 1.998–2.052(1); 2.000–2.053(1) | 2.000–2.056(2); 1.994–2.062(2) |
| (av.)                               | 2.039; 2.044                   | 2.032; 2.035                   | 2.030; 2.033                   | 2.035; 2.035                   |
| Fe–C(101)                           | 1.992(2)                       | 1.994(2)                       | 1.998(1)                       | 2.000(2)                       |
| Fe–C(201)                           | 2.003(2)                       | 2.002(1)                       | 2.000(1)                       | 1.994(2)                       |
| C(11)–O(1)                          | 1.432(2)                       | 1.447(2)                       | 1.440(2)                       | 1.447(2)                       |
| C(11)–C(12)                         | 1.478(2)                       | 1.470(2)                       | 1.470(2)                       | 1.476(3)                       |
| C(11)–C(101)                        | 1.497(2)                       | 1.508(2)                       | 1.511(2)                       | 1.509(2)                       |
| C(12)–C(13)                         | 1.204(2)                       | 1.200(2)                       | 1.195(2)                       | 1.177(3)                       |
| C(13)–Si(1)                         | 1.854(2)                       | 1.845(2)                       |                                |                                |
| C(21)–O(1)                          | 1.460(2)                       | 1.447(2)                       | 1.443(2)                       | 1.442(2)                       |
| C(21)–C(22)                         | 1.462(2)                       | 1.481(2)                       | 1.470(2)                       | 1.470(2)                       |
| C(21)–C(201)                        | 1.502(2)                       | 1.513(2)                       | 1.504(2)                       | 1.507(2)                       |
| C(22)–C(23)                         | 1.192(2)                       | 1.197(2)                       | 1.188(2)                       | 1.177(2)                       |
| C(23)–Si(2)                         | 1.831(2)                       | 1.843(2)                       |                                |                                |
| <i>Bond angles (°)</i>              |                                |                                |                                |                                |
| C(11)–O(1)–C(21)                    | 114.8(1)                       | 115.0(1)                       | 113.55(9)                      | 115.4(1)                       |
| C(12)–C(11)–O(1)                    | 107.4(1)                       | 107.5(1)                       | 105.8(1)                       | 111.2(1)                       |
| C(101)–C(11)–O(1)                   | 112.0(1)                       | 112.5(1)                       | 113.26(9)                      | 113.3(1)                       |
| C(12)–C(11)–C(101)                  | 109.8(1)                       | 110.6(1)                       | 111.4(1)                       | 111.5(2)                       |
| C(11)–C(12)–C(13)                   | 176.0(2)                       | 175.0(2)                       | 179.5(2)                       | 177.9(2)                       |
| C(12)–C(13)–Si(1)                   | 175.4(2)                       | 175.7(2)                       |                                |                                |
| C(22)–C(21)–O(1)                    | 104.9(1)                       | 110.8(1)                       | 113.7(1)                       | 105.5(1)                       |
| C(201)–C(21)–O(1)                   | 114.2(1)                       | 114.4(1)                       | 105.9(1)                       | 113.8(1)                       |
| C(22)–C(21)–C(201)                  | 108.3(1)                       | 112.8(1)                       | 111.1(1)                       | 111.7(1)                       |
| C(21)–C(22)–C(23)                   | 173.5(2)                       | 176.8(2)                       | 177.5(2)                       | 178.1(2)                       |
| C(22)–C(23)–Si(2)                   | 174.2(2)                       | 173.5(2)                       |                                |                                |
| Cp <sup>0</sup> –Fe–Cp <sup>0</sup> | 172.0                          | 172.4                          | 172.7                          | 171.9                          |



**Fig. 5.** Plot of the cation of cyclic vinylidene **5**.

**1,1'-Fc{C(O)C≡CSiMe<sub>3</sub>}[C(O)C≡CH] **4**** ( $R_f = 0.31$ ), dark red solid (100 mg, 15%). Anal. Calc. for  $C_{19}H_{18}FeO_2Si$ : C, 62.99; H, 5.01; M, 362. Found: C, 63.24; H, 5.06%. IR (nujol)/ $cm^{-1}$ :  $\nu(\equiv CH)$  3262 m,  $\nu(C=C)$  2153w, 2097 m,  $\nu(C=O)$  1625s.  $^1H$  NMR:  $\delta$  0.33 (s, 9H, SiMe<sub>3</sub>), 3.34 (s, 1H, C≡CH), 4.67 (s, 4H, C<sub>5</sub>H<sub>4</sub> of Fc), 4.99 (s, 4H, C<sub>5</sub>H<sub>4</sub> of Fc).  $^{13}C$  NMR:  $\delta$  -0.60 (SiMe<sub>3</sub>), 72.22, 72.31, 75.41, 75.69 (C<sub>5</sub>H<sub>4</sub> of Fc), 78.22 (C≡CH), 80.96 (C≡C), 81.12 (*ipso* of Fc), 81.57 (*ipso* of Fc), 98.12 (C≡C), 101.46 (C≡C), 179.33 (C=O), 179.75 (C=O). ES-MS ( $m/z$ ): 385, [M+Na]<sup>+</sup>; 363, [M+H]<sup>+</sup>.

#### 4.4.3. Reaction of Fc{1-C(O)C≡CSiMe<sub>3</sub>}[1'-C(O)C≡CH] with RuCl(dppe)Cp

A mixture of Fc{1-C(O)C≡CSiMe<sub>3</sub>}[1'-C(O)C≡CH] (37 mg, 0.10 mmol), RuCl(dppe)Cp (60 mg, 0.10 mmol) and Na[BPh<sub>4</sub>] (115 mg, 0.33 mmol) in MeOH (20 mL) was heated at reflux point for 30 min. After cooling, the resulting precipitate was filtered off, washed with MeOH and hexane, and dried to afford cyclic vinylidene complex **5** (60 mg, 51%). This complex was further purified by either preparative t.l.c. (acetone-CH<sub>2</sub>Cl<sub>2</sub>, 5/95;  $R_f = 0.32$ ) or

**Table 3**  
Selected bond parameters for the cation in cyclic vinylidene 5.

| Bond distances (Å) |                                   | Bond angles (°)                     |           |
|--------------------|-----------------------------------|-------------------------------------|-----------|
| Ru–P(1)            | 2.2988(2)                         | P(1)–Ru–P(2)                        | 82.26(1)  |
| Ru–P(2)            | 2.2970(2)                         | P(1)–Ru–C(1)                        | 82.93(2)  |
| Ru–C(cp)           | 2.256–2.280(1)                    | P(2)–Ru–C(1)                        | 91.34(3)  |
| (av.)              | 2.27                              | Ru–C(1)–C(2)                        | 175.93(7) |
| Ru–C(1)            | 1.845(1)                          | C(1)–C(2)–C(3)                      | 119.78(9) |
| C(1)–C(2)          | 1.321(1)                          | C(1)–C(2)–C(6)                      | 118.02(8) |
| C(2)–C(3)          | 1.476(1)                          | C(3)–C(2)–C(6)                      | 121.73(9) |
| C(2)–C(6)          | 1.526(1)                          | C(2)–C(3)–C(4)                      | 128.91(9) |
| C(3)–C(4)          | 1.335(2)                          | C(3)–C(4)–C(5)                      | 127.17(9) |
| C(4)–C(5)          | 1.497(2)                          | C(4)–C(5)–O(5)                      | 122.45(9) |
| C(5)–O(5)          | 1.215(1)                          | C(4)–C(5)–C(201)                    | 114.95(8) |
| C(5)–C(201)        | 1.467(1)                          | C(201)–C(5)–O(5)                    | 122.5(1)  |
| C(6)–O(6)          | 1.220(1)                          | C(2)–C(6)–O(6)                      | 119.29(8) |
| C(6)–C(301)        | 1.462(1)                          | C(2)–C(6)–C(301)                    | 119.12(7) |
| Fe–C(cp)           | 2.021–2.067(1);<br>2.026–2.065(1) | C(301)–C(6)–O(6)                    | 121.58(8) |
| (av.)              | 2.046; 2.046                      | Cp <sup>0</sup> –Fe–Cp <sup>0</sup> | 178.8     |
| Fe–C(201)          | 2.021(1)                          |                                     |           |
| Fe–C(301)          | 2.026(1)                          |                                     |           |

**Table 4**  
Some electrochemical data.

| Compounds  | Oxidation (V)  |                     | Reduction (V)  |
|------------|----------------|---------------------|----------------|
|            | E <sub>1</sub> | E <sub>2</sub>      | E <sub>3</sub> |
| <b>2a</b>  | +0.54          |                     |                |
| <b>2b</b>  | +0.55          |                     |                |
| <b>3</b>   | +1.07          |                     | –1.42 (irrev.) |
| <b>4</b>   | +1.09          |                     | –1.48 (irrev.) |
| <b>5</b>   | +0.88 (irrev.) | +0.92               | –1.40 (irrev.) |
| <b>6a</b>  | +0.62          |                     |                |
| <b>6b</b>  | +0.63          |                     |                |
| <b>7a</b>  | +0.70          |                     |                |
| <b>7b</b>  | +0.64          |                     |                |
| <b>8a</b>  | +0.40          | +0.66               | +0.72          |
| <b>8b</b>  | +0.41          | +0.63               | +0.76          |
| <b>9a</b>  | +0.56 (2-e)    | +0.65 (1-e)         |                |
| <b>9b</b>  | +0.54 (3-e)    |                     |                |
| <b>10</b>  | +0.70 (2-e)    | +1.11 (1-e; irrev.) |                |
| <b>11a</b> | +0.56 (2-e)    | +0.65 (1-e)         |                |
| <b>11b</b> | +0.59 (3-e)    |                     |                |

crystallisation (CHCl<sub>3</sub>). Anal. Calc. for C<sub>71</sub>H<sub>59</sub>BFeO<sub>2</sub>P<sub>2</sub>Ru·1.75CHCl<sub>3</sub>: C, 63.27; H, 4.43; M (unsolvated), 855. Found: C, 63.53; H, 4.49%. IR (nujol)/cm<sup>-1</sup>: ν(C=O) 1662s, 1636 m, ν(C=C), 1599 m, 1572s. <sup>1</sup>H NMR (d<sub>6</sub>-acetone): δ 3.17–3.33 (m, 4H, 2 x CH<sub>2</sub> of dppe), 4.52–4.55 (m, 6H, FeC<sub>5</sub>H<sub>4</sub>), 4.63 (s, 2H, FeC<sub>5</sub>H<sub>4</sub>), 4.89 [d, J = 12.3 Hz, 1H, C(O)CH=CH], 5.07 [d, J = 12.3 Hz, 1H, C(O)CH=CH], 5.92 (s, 5H, RuCp), 6.75–6.80 (m, 4H, Ph), 6.90–6.95 (m, 8H, Ph), 7.27–7.49 (m, 24H, Ph), 7.64–7.71 (m, 4H, Ph). <sup>13</sup>C NMR (d<sub>6</sub>-acetone): δ 28.52–29.15 (m, CH<sub>2</sub> of dppe), 72.70 (br), 75.74, 76.23, 81.53 (ipso of Fc), 82.94 (ipso of Fc), 94.37 (RuCp), 118.46 [C(O)CH=CH], 122.84, 125.48 [C(O)CH=CH], 126.57–126.61 (m), 130.46–130.59 (m), 132.14 (Ru=C=C), 132.68–132.79 (m), 134.27–134.33 (m), 137.62, 164.50–166.47 (m), 184.06 (C=O), 195.55 (C=O), 345.58–345.85 (m, Ru=C=C). <sup>31</sup>P NMR (d<sub>6</sub>-acetone): δ 78.0 (dppe). ES-MS (m/z): 855, M<sup>+</sup>. X-ray quality crystals were obtained from chloroform.

#### 4.4.4. Cyclophanes *cis*- and *trans*-Fc{CH(C≡CSiMe<sub>3</sub>)<sub>2</sub>O} 6

A mixture of 1,1'-Fc{CH(OH)C≡CSiMe<sub>3</sub>}<sub>2</sub> (336 mg, 0.767 mmol) and pTSA (3 mg, 0.02 mmol) in benzene (100 mL) was heated at reflux point with the use of a Dean-Stark trap for 30 min. The cooled solution was passed quickly through a pad of silica gel and the solvent removed under vacuum. The crude residue was subsequently purified by flash chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>-hexane, 2/3) to afford two isomeric cyclophanes.

*cis*-Fc{CH(C≡CSiMe<sub>3</sub>)<sub>2</sub>O} *cis*-**6a**: (R<sub>f</sub> = 0.46) as a light yellow solid (94 mg, 29%). Anal. Calc. for C<sub>22</sub>H<sub>28</sub>FeOSi<sub>2</sub>: C, 62.84; H, 6.71; M, 420. Found: C, 63.11; H, 6.70%. IR (nujol) ν(C≡C)/cm<sup>-1</sup>: 2180 m. <sup>1</sup>H NMR: δ 0.17 (s, 18H, SiMe<sub>3</sub>), 4.09–4.11 (m, 2H), 4.23–4.25 (m, 2H), 4.32–4.33 (m, 2H), 4.42 (s, 2H, CHO), 4.49–4.50 (m, 2H). <sup>13</sup>C NMR: δ –0.24 (SiMe<sub>3</sub>), 67.00 (CHO), 69.19, 71.23, 86.25 (ipso of Fc), 91.22 (C≡C), 101.85 (C≡C). ES-MS (m/z): 863, [2M+Na]<sup>+</sup>; 443, [M+Na]<sup>+</sup>; 421, [M+H]<sup>+</sup>. X-ray quality crystals were grown from CH<sub>2</sub>Cl<sub>2</sub>/MeOH.

*trans*-Fc{CH(C≡CSiMe<sub>3</sub>)<sub>2</sub>O} *trans*-**6b**: (R<sub>f</sub> = 0.39) as a yellow solid (142 mg, 44%). Anal. Calc. for C<sub>22</sub>H<sub>28</sub>FeOSi<sub>2</sub>: C, 62.84; H, 6.71; M, 420. Found: C, 62.99; H, 6.72%. IR (nujol)/cm<sup>-1</sup>: ν(C≡C) 2177 m. <sup>1</sup>H NMR: δ 0.23 (s, 18H, SiMe<sub>3</sub>), 4.16–4.17 (m, 4H), 4.27–4.28 (m, 2H), 4.47–4.48 (m, 2H), 5.16 (s, 2H, CHO). <sup>13</sup>C NMR: δ –0.12 (SiMe<sub>3</sub>), 60.67 (CHO), 69.45, 69.83, 69.98, 70.19, 85.07 (ipso of Fc), 91.84 (C≡C), 101.50 (C≡C). ES-MS (m/z): 443, [M+Na]<sup>+</sup>; 438, [M+H<sub>3</sub>O]<sup>+</sup>; 421, [M+H]<sup>+</sup>; 420, M<sup>+</sup>. X-ray quality crystals were grown from CH<sub>2</sub>Cl<sub>2</sub>/MeOH.

#### 4.4.5. Cyclophanes *cis*- and *trans*-Fc{CH(C≡CH)}<sub>2</sub>O 7

*cis*-Fc{CH(C≡CH)}<sub>2</sub>O **7a**. A solution of *cis*-Fc{CH(C≡CSiMe<sub>3</sub>)<sub>2</sub>O} **6a** (62 mg, 0.15 mmol) and KF (33 mg, 0.57 mmol) in 75% MeOH/thf (10 mL) was stirred for 16 h at r.t. Solvent was removed under vacuum and the crude residue was taken up in Et<sub>2</sub>O and purified through a short pad of silica gel. Solvent was removed to afford pure *cis*-Fc{CH(C≡CH)}<sub>2</sub>O **7a** (38 mg, 93%) as a yellow solid. R<sub>f</sub> = 0.22 (40% CH<sub>2</sub>Cl<sub>2</sub>/hexane). Anal. Calc. for C<sub>16</sub>H<sub>12</sub>FeO: C, 69.60; H, 4.38; M, 276. Found: C, 69.33; H, 4.37%. IR (nujol)/cm<sup>-1</sup>: ν(≡CH) 3292 m, 3272 m, ν(C≡C) 2125w. <sup>1</sup>H NMR: δ 2.62 (s, 2H, C≡CH), 4.13 (s, 2H), 4.27 (s, 2H), 4.35 (s, 2H), 4.45 (d, J = 2.1 Hz, 2H), 4.51 (s, 2H). <sup>13</sup>C NMR: δ 66.12 (–CHO–), 66.99, 69.46, 71.15, 71.41, 74.62 (C≡CH), 80.72 (C≡CH), 85.67 (ipso of Fc). ES-MS (m/z): 299, [M+Na]<sup>+</sup>. X-ray quality crystals were obtained from Et<sub>2</sub>O/hexane.

*trans*-Fc{CH(C≡CH)}<sub>2</sub>O **7b**. A solution of *trans*-Fc{CH(C≡CSiMe<sub>3</sub>)<sub>2</sub>O} **6b** (55 mg, 0.13 mmol) and KF (23 mg, 0.40 mmol) in 75% MeOH/thf (10 mL) was stirred for 16 h at r.t. Solvent was removed under vacuum and the crude residue was taken up in Et<sub>2</sub>O and purified through a short pad of silica gel. Solvent was removed to afford pure *trans*-Fc{CH(C≡CH)}<sub>2</sub>O **7b** (34 mg, 95%) as a yellow solid. R<sub>f</sub> = 0.28 (40% CH<sub>2</sub>Cl<sub>2</sub>/hexane). Anal. Calc. for C<sub>16</sub>H<sub>12</sub>FeO: C, 69.60; H, 4.38; M, 276. Found: C, 67.67; H, 4.31%. IR (nujol)/cm<sup>-1</sup>: ν(≡CH) 3277 m, ν(C≡C) 2116w. <sup>1</sup>H NMR: δ 2.62 (d, J = 2.1 Hz, 2H, C≡CH), 4.18–4.19 (m, 4H), 4.31 (s, 2H), 4.50 (s, 2H), 5.18 (d, J = 2.1 Hz, 2H, CHO). <sup>13</sup>C NMR: δ 60.25 (CHO), 69.54, 70.16, 70.42, 74.87 (C≡CH), 80.01 (C≡CH), 84.54 (ipso of Fc). ES-MS (m/z): 299, [M+Na]<sup>+</sup>. X-ray quality crystals were obtained from Et<sub>2</sub>O/hexane.

#### 4.4.6. *cis*- and *trans*-Fc{CH(C<sub>2</sub>H[Co<sub>2</sub>(μ-dppm)(CO)<sub>4</sub>]}<sub>2</sub>O 8

*cis*-Fc{CH(C<sub>2</sub>H[Co<sub>2</sub>(μ-dppm)(CO)<sub>4</sub>]}<sub>2</sub>O **8a**. A solution of *cis*-Fc{CH(C≡CH)}<sub>2</sub>O **7a** (21 mg, 0.083 mmol) and Co<sub>2</sub>(μ-dppm)(CO)<sub>6</sub> (120 mg, 0.18 mmol) in dry thf (10 mL) was heated at reflux point for 2 h. Solvent was removed under vacuum and the crude residue was taken up in CH<sub>2</sub>Cl<sub>2</sub> and passed very quickly through a short neutral alumina column. Note that the complex decomposes rapidly when placed onto adsorbents such as alumina or silica. Solvent was removed and the residue subsequently crystallised from Et<sub>2</sub>O/hexane at –20 °C to give *cis*-Fc{CH(C<sub>2</sub>H[Co<sub>2</sub>(μ-dppm)(CO)<sub>4</sub>]}<sub>2</sub>O **8a** as a maroon solid (35 mg, 28%). Anal. Calc. for C<sub>74</sub>H<sub>56</sub>Co<sub>4</sub>FeO<sub>5</sub>P<sub>4</sub>: C, 59.07; H, 3.75; M, 1504. Found: C, 59.40; H, 4.07. IR (nujol)/cm<sup>-1</sup>: ν(CO) 2022 m, 1992s, 1962s. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 2.82–2.88 (m, 2H, CH<sub>2</sub> of dppm), 3.16–3.21 (m, 2H, CH<sub>2</sub> of dppm), 4.00, 4.14, 4.36, 4.86 (4 x s, 4 x 2H, C<sub>5</sub>H<sub>4</sub>Fe), 5.48 (t, J = 5.4 Hz, 2H, CHO), 5.95 (t, J = 6.6 Hz, 2H, Co<sub>2</sub>C<sub>2</sub>H), 6.84–6.87 (m, 20H, Ph), 7.31 (s, 16H, Ph), 7.38 (s, 4H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 41.47–41.60 (m, CH<sub>2</sub> of dppm),



**Table 5**  
Crystal data and refinement details.

| Compounds                                  | 3  | 5   | 6a   | 6b   | 7a                                  | 7b                                  | 10  |
|--|--|---|--|--|-------------------------------------|-------------------------------------|---|
| Formula                                    | C <sub>22</sub> H <sub>26</sub> FeO <sub>5</sub> Si <sub>2</sub> | C <sub>71</sub> H <sub>59</sub> BFeO <sub>2</sub> Ru <sub>2</sub> ·2CHCl <sub>3</sub> | C <sub>22</sub> H <sub>28</sub> FeO <sub>5</sub> Si <sub>2</sub> | C <sub>22</sub> H <sub>28</sub> FeO <sub>5</sub> Si <sub>2</sub> | C <sub>16</sub> H <sub>12</sub> FeO | C <sub>16</sub> H <sub>12</sub> FeO | C <sub>36</sub> H <sub>26</sub> Fe <sub>3</sub> O <sub>2</sub> ·CH <sub>2</sub> Cl <sub>2</sub> |
| MW   | 434.46   | 1412.59   | 420.47   | 420.47   | 276.11                              | 276.11                              | 743.04  |
| Crystal system                             | Triclinic  | Triclinic   | Monoclinic   | Monoclinic   | Monoclinic                          | Orthorhombic                        | Monoclinic  |
| Space group                                | P $\bar{1}$  | P $\bar{1}$   | P2 <sub>1</sub> /c   | P2 <sub>1</sub> /c   | P2 <sub>1</sub> /c                  | Pbcm                                | C2/c  |
| a (Å)                                      | 5.8512(2)  | 15.2321(4)  | 5.7913(2)  | 16.6386(4)   | 15.8876(3)                          | 30.221(2)                           | 24.4883(4)  |
| b (Å)                                      | 6.7236(3)  | 15.3883(3)  | 12.0344(4)   | 5.8000(1)  | 7.2984(1)                           | 5.8952(2)                           | 11.6081(2)  |
| c (Å)                                      | 15.5543(7)   | 15.6891(2)  | 31.7705(10)  | 23.4101(6)   | 10.6878(2)                          | 13.1171(9)                          | 14.5528(3)  |
| $\alpha$ (°)                               | 80.244(4)  | 84.483(1)   |  |  |                                     |                                     |   |
| $\beta$ (°)                                | 89.919(4)  | 66.016(2)   |  |  |                                     |                                     |   |
| $\gamma$ (°)                               | 69.491(4)  | 70.895(2)   |  |  |                                     |                                     |   |
| V (Å <sup>3</sup> )                        | 563.7  | 3172.0  | 90.742(3)  | 101.310(2)   | 104.202(2)                          |                                     | 134.654(2)  |
| $\rho_c$                                   | 1.280  | 1.479   | 2.214.1  | 2.215.3  | 1.201.4                             | 2.336.9                             | 2.942.8   |
| Z  | 1  | 2   | 4  | 4  | 4                                   | 8                                   | 4   |
| 2 $\theta_{max}$ (°)                       | 62   | 82  | 66   | 64   | 82                                  | 66                                  | 67  |
| $\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> ) | 0.79   | 0.82  | 0.80   | 0.80   | 1.237                               | 1.271                               | 13.65 (μ(Cu K $\alpha$ ))   |
| T <sub>min</sub> /max                      | 0.905/0.982  | 0.94/1  | 0.89/1   | 0.88/1   | 0.84/1                              | 0.96/1                              | 0.204/0.874   |
| Crystal dimensions (mm <sup>3</sup> )      | 0.23 × 0.07 × 0.02   | 0.27 × 0.27 × 0.13  | 0.30 × 0.06 × 0.03   | 0.52 × 0.06 × 0.04   | 0.21 × 0.19 × 0.16                  | 0.37 × 0.09 × 0.03                  | 0.17 × 0.11 × 0.04  |
| N <sub>tot</sub>                           | 7193   | 102 153   | 29 555   | 34 175   | 29 982                              | 29 028                              | 16 740  |
| N (R <sub>int</sub> )                      | 3579 (0.083)   | 40 321 (0.036)  | 7549 (0.061)   | 7277 (0.049)   | 7776 (0.041)                        | 4306 (0.058)                        | 2626 (0.045)  |
| N <sub>o</sub>                             | 1878   | 20 338  | 5017   | 4349   | 5475                                | 2715                                | 2354  |
| R <sub>1</sub> [I > 2 $\sigma$ (I)]        | 0.053  | 0.042   | 0.039  | 0.036  | 0.039                               | 0.038                               | 0.047   |
| wR <sub>2</sub> (all data)                 | 0.084  | 0.096   | 0.083  | 0.078  | 0.114                               | 0.078                               | 0.140   |

67.24, 68.76, 70.45, 71.94 (4 × C<sub>5</sub>H<sub>4</sub>Fe), 75.16 (broad, Co<sub>2</sub>CCH), 80.52 (CHO), 91.59 (*ipso* of Fc), 102.05 (broad, Co<sub>2</sub>CCH), 127.55–128.44 (m, Ph), 129.30–129.54 (m, Ph), 132.02–132.48 (m, Ph), 137.31–137.59 (m, Ph), 204.63, 208.05 [2 × Co(CO)]. <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  44.0 (dppm). ES-MS (*m/z*): 1527, [M+Na]<sup>+</sup>.

*trans*-Fc{CH(C $\equiv$ CH)}<sub>2</sub>O **7b**. A solution of *trans*-Fc{CH(C $\equiv$ CH)}<sub>2</sub>O **7b** (21 mg, 0.076 mmol) and Co<sub>2</sub>( $\mu$ -dppm)(CO)<sub>6</sub> (105 mg, 0.16 mmol) in dry thf (10 mL) was heated at reflux point for 2 h. Solvent was removed under vacuum and the crude residue was extracted with MeOH. Solvent was removed and the crude residue taken up in Et<sub>2</sub>O, filtered and layered with hexane and left to crystallise at –20 °C overnight giving *trans*-Fc{CH(C<sub>2</sub>H[Co<sub>2</sub>( $\mu$ -dppm)(CO)<sub>4</sub>)]<sub>2</sub>O **8b** as a maroon solid (61 mg, 53%). Due to the instability of the complex, it was not possible to employ chromatography in the purification of this system. Anal. Calc. for C<sub>74</sub>H<sub>56</sub>Co<sub>4</sub>FeO<sub>9</sub>P<sub>4</sub>: C, 59.07; H, 3.75; M, 1504. Found C, 59.23; H, 4.00%. IR (nujol)/cm<sup>-1</sup>:  $\nu$ (CO) 2019 m, 1999s, 1959s. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  2.85–2.97 (m, 2H, CH<sub>2</sub> of dppm), 3.20–3.35 (m, 2H, CH<sub>2</sub> of dppm), 4.12, 4.58, 5.07 (3 × s, 4H + 2H + 2H, C<sub>5</sub>H<sub>4</sub>Fe), 6.16 (t, *J* = 6.6 Hz, 2H, CHO), 6.34 (t, *J* = 6.3 Hz, 2H, Co<sub>2</sub>C<sub>2</sub>H), 6.89 (s, 20H, Ph), 7.37 (s, 16H, Ph), 7.86 (s, 4H, Ph). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  41.59–41.97 (m, CH<sub>2</sub> of dppm), 69.24, 69.49, 69.94, 71.66 (4 × C<sub>5</sub>H<sub>4</sub>Fe), 73.46 (CHO), 76.05 (broad, Co<sub>2</sub>CC–H), 90.23 (*ipso* of Fc), 100.96 (broad, Co<sub>2</sub>CCH), 129.38–129.49 (m, Ph), 131.31–132.48 (m, Ph), 136.86–137.60 (m, Ph), 204.48, 207.83 [2 × Co(CO)]. <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  44.1 (dppm). ES-MS (*m/z*): 1527, [M+Na]<sup>+</sup>.

#### 4.5. Ferrocenylethynyl derivatives

##### 4.5.1. 1,1'-Fc{CH(OH)C $\equiv$ Cfc}<sub>2</sub> **9**

To a solution of FcC $\equiv$ CH (320 mg, 1.52 mmol) in dry thf (50 mL) at –78 °C was added *n*-BuLi (0.80 mL, 1.6 M in hexanes, 1.27 mmol) and the resulting solution was stirred for 30 min. 1,1'-Fc'(CHO)<sub>2</sub> (123 mg, 0.51 mmol) was added and the mixture was warmed until all the solids had dissolved. Cooling to –78 °C and stirring for a further 30 min. was followed by quenching the mixture with saturated aqueous NH<sub>4</sub>Cl. The crude biphasic mixture was extracted twice with Et<sub>2</sub>O and the combined organic fraction was dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and solvent was removed under vacuum. The crude residue was purified by column chromatography (silica gel, Et<sub>2</sub>O–hexane, 3/2) to afford diastereomers of 1,1'-Fc{CH(OH)C $\equiv$ Cfc}<sub>2</sub> **9a, b**.

Isomer **9a** (*R<sub>f</sub>* = 0.47) was obtained as an orange solid (174 mg, 52%). Anal. Calc. for C<sub>36</sub>H<sub>30</sub>Fe<sub>3</sub>O<sub>2</sub>: C, 65.25; H, 4.57; M, 662. Found: C, 65.25; H, 4.63%. IR (nujol)/cm<sup>-1</sup>:  $\nu$ (OH) 3289 (br),  $\nu$ (C $\equiv$ C) 2225 m. <sup>1</sup>H NMR (d<sub>6</sub>-dmsO):  $\delta$  4.25–4.33 (m, 20H), 4.43 (s, 2H), 4.50–4.51 (m, 4H), 5.33 (d, *J* = 6.6 Hz, 2H, CHOH), 5.73 (d, *J* = 6.6 Hz, 2H, CHOH). <sup>13</sup>C NMR (d<sub>6</sub>-dmsO):  $\delta$  59.73 (CHOH), 64.91 (*ipso* of FcC $\equiv$ C), 67.43, 68.63, 68.70, 68.82, 68.93, 69.66, 70.98, 79.18, 81.51 (C $\equiv$ C), 87.42 (C $\equiv$ C), 90.30 (*ipso* of Fc). ES-MS (*m/z*): 685, [M+Na]<sup>+</sup>; 662, M<sup>+</sup>; 645, [M–OH]<sup>+</sup>.

Isomer **9b** (*R<sub>f</sub>* = 0.41) was an orange solid (142 mg, 42%). Anal. Calc. for C<sub>36</sub>H<sub>30</sub>Fe<sub>3</sub>O<sub>2</sub>: C, 65.25; H, 4.57; M, 662. Found: C, 65.65; H, 4.69%. IR (nujol)/cm<sup>-1</sup>:  $\nu$ (OH) 3288 (br),  $\nu$ (C $\equiv$ C) 2220w. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300):  $\delta$  3.44 (s, 2H, CHOH), 3.90–3.91 (m, 4H), 4.05–4.06 (m, 2H), 4.12–4.14 (m, 12H), 4.41–4.42 (m, 2H), 4.44–4.45 (m, 2H), 5.45 (s, 2H, CHOH). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  61.86 (CHOH), 65.78 (*ipso* of FcC $\equiv$ C), 68.12, 68.98, 69.34, 69.41, 69.46, 70.73, 72.30, 72.33, 84.18 (C $\equiv$ C), 87.52 (C $\equiv$ C), 92.26 (*ipso* of Fc). ES-MS (*m/z*): 685, [M+Na]<sup>+</sup>; 662, M<sup>+</sup>; 645, [M–OH]<sup>+</sup>.

##### 4.5.2. 1,1'-Fc{C(O)C $\equiv$ Cfc}<sub>2</sub> **10**

MnO<sub>2</sub> (1.0 g) was added to a rapidly stirred solution of 1,1'-Fc{CH(OH)C $\equiv$ Cfc}<sub>2</sub> (101 mg, 0.153 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and the resulting suspension was stirred vigorously for 30 min. The

solution was filtered and the crude filtrate passed through a short pad of silica gel, eluting with  $\text{CH}_2\text{Cl}_2$ . The solvent was reduced in volume and layered carefully with hexane. The diketone 1,1'-Fc{C(O)C≡CFC}\_2 **10** crystallised overnight as dark red crystals (92 mg, 92%).  $R_f = 0.61$  ( $\text{CH}_2\text{Cl}_2$ ). Anal. Calc. for  $\text{C}_{36}\text{H}_{26}\text{Fe}_3\text{O}_2 \cdot \text{CH}_2\text{Cl}_2$ : C, 59.81; H, 4.31; M, 658. Found: C, 59.87; H, 4.11%. IR (nujol)/ $\text{cm}^{-1}$ :  $\nu(\text{C}=\text{C})$  2189 m, 2162 m,  $\nu(\text{C}=\text{O})$  1615s.  $^1\text{H}$  NMR:  $\delta$  4.32 (s, 10H), 4.44 (s, 4H), 4.69 (s, 8H), 5.06 (s, 4H).  $^{13}\text{C}$  NMR:  $\delta$  60.45 (*ipso* of Fc), 70.49, 70.72, 71.93 (br), 73.06 (br), 74.26 (br), 82.13 (*ipso* of Fc), 85.82 (C≡C), 94.07 (C≡C), 179.98 (C=O). ES-MS ( $m/z$ ): 681,  $[\text{M}+\text{Na}]^+$ .

#### 4.5.3. Cyclophanes *cis*- and *trans*-Fc{CH(C≡CFC)}\_2O **11**

A mixture of 1,1'-Fc{CH(OH)C}\_2FC}\_2 **9** (135 mg, 0.20 mmol) and pTSA (2 mg, 0.01 mmol) in benzene (100 mL) was heated at reflux point with the use of a Dean-Stark trap for 30 min. The cooled solution was passed quickly through a pad of silica gel and the solvent removed under vacuum. The crude residue was subsequently purified by preparative t.l.c. ( $\text{CH}_2\text{Cl}_2$ -hexane, 7/3) to afford isomeric cyclophanes *cis*- and *trans*-Fc{CH[C≡CFC]}\_2O **11a, b**.

*cis*-Fc{CH[C≡CFC]}\_2O **11a**: ( $R_f = 0.78$ ) as a yellow solid (19 mg, 13%). IR (nujol)/ $\text{cm}^{-1}$ :  $\nu(\text{C}=\text{C})$  2252w, 2235w, 2228w.  $^1\text{H}$  NMR:  $\delta$  4.13–4.19 (m, 16H), 4.28 (broad s, 2H), 4.39–4.42 (m, 6H), 4.58–4.59 (m, 2H), 4.63 (s, 2H, CHO).  $^{13}\text{C}$  NMR:  $\delta$  64.65 (*ipso* of Fc), 67.08, 67.19 (CHO), 68.53, 69.11, 69.84, 71.04, 71.17, 71.45, 82.61 (C≡C), 85.14 (C≡C), 86.89 (*ipso* of Fc). ES-MS ( $m/z$ ): 667,  $[\text{M}+\text{Na}]^+$ ; 645,  $[\text{M}+\text{H}]^+$ ; 644,  $\text{M}^+$ . HR-MS: calcd ( $\text{C}_{36}\text{H}_{28}\text{Fe}_3\text{O}$ ): 644.0188, found: 644.0238.

*trans*-Fc{CH[C≡CFC]}\_2O **11b**: ( $R_f = 0.70$ ) as a yellow solid (110 mg, 72%). Anal. Calc. for  $\text{C}_{36}\text{H}_{28}\text{Fe}_3\text{O}$ : C, 67.13; H, 4.38; M, 643. Found: C, 67.53; H, 4.69%. IR (nujol)/ $\text{cm}^{-1}$ :  $\nu(\text{C}=\text{C})$  2221 m.  $^1\text{H}$  NMR:  $\delta$  4.24 (broad s, 18H), 4.38 (s, 2H), 4.49 (s, 4H), 4.58 (s, 2H), 5.36 (s, 2H, CHO).  $^{13}\text{C}$  NMR:  $\delta$  61.06 (CHO), 64.44 (*ipso* of Fc), 68.71, 69.55, 69.72, 69.91, 70.13, 71.57, 71.61, 81.97 (C≡C), 85.67 (C≡C), 85.84 (*ipso* of Fc). ES-MS ( $m/z$ ): 667,  $[\text{M}+\text{Na}]^+$ ; 645,  $[\text{M}+\text{H}]^+$ ; 644,  $\text{M}^+$ .

#### 4.6. Structure determinations

The crystal data for compounds **3**, **6a**, **6b**, **7a**, **7b** and **10** are summarised in Table 5 with the structures depicted in Figs. 1–5, where ellipsoids have been drawn at the 50% probability level and hydrogen atoms with arbitrary radii of 0.1 Å. Selected coordination geometries are given in Tables 1–3. Crystallographic data for the structures were collected at 100 K (150 K for **5**) on an Oxford Diffraction Gemini (for **3**, **6a**, **7a**, **10**) or Xcalibur (for **5**, **6b**, **7b**) diffractometers fitted with monochromated Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å (Cu  $K\alpha$ ,  $\lambda = 1.54178$  Å, for **10**) radiation yielding a total of  $N_{\text{tot}}$  reflections, these merging to  $N$  unique after multi-scan absorption corrections ( $R_{\text{int}}$  cited), with  $N_0$  reflections having  $I > 2\sigma(I)$ . The structures were refined against  $F^2$  with full-matrix least-squares using the program SHELXL-97 [17]. In general, all H atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the isotropic displacement param-

eter of the parent atom. Anisotropic displacement parameters, except where stated, were employed for all non-hydrogen atoms. In **5**, one  $\text{CH}_2\text{Cl}_2$  solvent molecule was modelled as being disordered over two sites with refined site occupancies of 0.6941(6) and its complement. The C atom of the minor component was refined with isotropic displacement parameters. The keto chains in **10** are disordered about the crystallographic 2 axis with site occupancies 0.58(1) and 1 – 0.58(1). The solvent  $\text{CH}_2\text{Cl}_2$  is also disordered with assigned site occupancies of 0.5.

#### Acknowledgements

We thank Professor Brian Nicholson (University of Waikato, Hamilton, New Zealand) for providing the mass spectra, the ARC for support of this work and Johnson Matthey plc, Reading, for a generous loan of  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ .

#### Appendix A. Supplementary material

CCDC 736657, 736658, 736659, 736660, 736661, 736662 and 736663 contain the supplementary crystallographic data for **3**, **5**, **6a**, **6b**, **7a**, **7b** and **10**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.024.

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