

1,1'-(1-Propene-1,3-diyl)-ferrocene: modified synthesis, crystal structure, and polymerisation behaviour

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Abstract

The dehydro[3](1,1')ferrocenophanes, 1,1'-(1-propene-1,3-diyl)-ferrocene (**3a**), and 1,1'-(3-phenyl-1-propene-1,3-diyl)-ferrocene (**3b**) were synthesised under Shapiro conditions from the tosylhydrazones of the corresponding α -oxo-[3](1,1')ferrocenophanes. Electrochemistry shows **3a** is oxidised at similar potential to ferrocene; according **3a** can be chemically oxidised using silver trifluoromethanesulfonate. The structure of **3a** shows a ring tilt of 11.3°. Attempts to polymerise **3a** using the ROMP initiator Mo(CHCMe₂Ph)[N(2,6-*i*Pr₂C₆H₃)] [OCMe(CF₃)₂]₂ led to a mixture of insoluble material and a soluble mixture of apparently cyclic oligomers (**[3a]_n**).

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1. Introduction

Recently there has been considerable interest in polymers incorporating ferrocene (and to a lesser extent other metallocenes) into their main chain [1–3]. Many of the best methods for making high molecular weight well-defined species involve the ring-opening of strained ferrocenophanes: [2]ferrocenophanes with C₂H₄ bridges have been polymerised thermally [4]; [1]ferrocenophanes with various heteroatom bridges have been polymerised thermally [5,6], anionically [7], or using transition-metal catalysts [8,9]; [3]ferrocenophanes with S₃ bridges have been converted to polymers through sulfur abstraction by phosphines [10]; and [2]ferrocenophanes [11] and [4]ferrocenophanes [12,13] with unsaturated hydrocarbon bridges have been polymerised using ROMP [14]. ROMP offers, under certain circumstances, possibilities to synthesize conjugated polymers, to obtain narrow molecular weight distributions, to control the nature of the end groups, to obtain well-defined block copolymers, and to incorporate a wide range of chemical

functionalities into polymers [15–19]. The use of ROMP to polymerise [3]ferrocenophanes with unsaturated bridges has not been reported; although the resulting polymers would not be conjugated, there are precedents suggesting that hydride could be abstracted from CH=CH–CH₂ bridges [20] to afford cationic polymers with the (CH)₃⁺ bridges facilitating interesting intermetallic interactions [20,21]. Here we report: an improved synthesis of 1,1'-(1-propene-1,3-diyl)-ferrocenes, i.e. dehydro[3](1,1')ferrocenophanes (**3**); the crystal structure of 1,1'-(1-propene-1,3-diyl)-ferrocene (**3a**); and preliminary studies of the behavior of **3a** when treated with ROMP initiators.

2. Experimental

2.1. General

Cyclic voltammograms were recorded using a glassy-carbon working electrode, a platinum wire auxiliary electrode and a silver wire pseudo-reference electrode. Measurements were made on deoxygenated THF solutions ca. 0.1 M in [^tBu₄N]⁺[PF₆]⁻. Potentials were

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referenced to the ferrocene/ferrocenium couple at 0 V by comparison to ferrocene under the same conditions. Gel-permeation chromatography (GPC) was carried out using PLgel Mixed-A columns calibrated with polystyrene narrow standards ($M_p = 580 - 11.6 \times 10^{-6}$) in THF, with toluene as a flow marker. The THF was degassed with helium and pumped at a rate of 1 ml min^{-1} at 30°C . The ROMP initiators, [Ru] and [Mo] were obtained from Strem, whilst other chemicals were obtained from Aldrich.

2.2. X-ray crystallography

An orange–yellow platy single crystal of **3a** ($\text{C}_{13}\text{H}_{12}\text{Fe}$, RMM = 224.09) of approximate dimensions $0.06 \times 0.18 \times 0.23 \text{ mm}$, grown by slow evaporation of a hexane solution, was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data (6520 reflections, $5.0^\circ \leq \theta \leq 27.5^\circ$) were measured using an Enraf-Nonius Kappa CCD diffractometer (graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). Intensity data were processed using the DENZO-SMN package [22]. The crystal was found to be orthorhombic, with $a = 7.5774(3) \text{ \AA}$, $b = 9.9886(4) \text{ \AA}$, $c = 12.5472(5) \text{ \AA}$, $V = 949.7 \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc}} = 1.567 \text{ g cm}^{-3}$, and $\mu = 1.536 \text{ mm}^{-1}$. Examination of the systematic absences of the intensity data showed the space group to be either $Pbnm$ or $Pbn2_1$. All attempts to solve the structure in the former space group were unsuccessful. The structure was solved in the space group $Pbn2_1$ using the direct-methods program SIR92 [22], which located all non-hydrogen atoms. Examination of the resulting model clearly showed no crystallographic mirror plane to be present, confirming the assignment of symmetry. A semi-empirical absorption correction was employed (minimum and maximum transmission coefficients of 0.70 and 0.91, respectively) based on equivalent reflections. Subsequent full-matrix least-squares refinement on F was carried out using the CRYSTALS Program Suite [23] (2167 unique reflections, $R_{\text{int}} = 0.035$, 1749 with $I > 3\sigma(I)$). Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. The resulting structure showed abnormal geometry of the alkene bridge, with the molecule appearing to have a highly symmetric structure with approximate point group $2mm$ (C_{2v}). In addition, the thermal parameters of the bridge C atoms seemed to be excessively large. The molecule was therefore modelled as disordered over two orientations related by a non-crystallographic mirror plane. The coordinates, isotropic thermal parameters and site occupancies of the bridging atoms were refined, with chemically equivalent bond lengths and angles restrained to their common means. The two positions for the disordered bridge closely overlap and consequently

it is uncertain whether the atomic coordinates are correct. Geometric parameters derived from the coordinates of these atoms should be regarded as unreliable. No attempt was made to model the disorder of the cyclopentadienyl fragments or of the iron atom. Determination of the absolute structure shows the crystal to be twinned by inversion (the refined value of the Flack Parameter is 0.52(3)). Hydrogen atoms were positioned geometrically after each cycle of refinement. A four-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give $R = 0.0275$, $R_w = 0.0288$, and $S = 1.0574$, with residual electron density minimum and maxima of -0.50 and 0.51 e \AA^{-3} , respectively. Full crystallographic data for the structural analysis of **3a** has been deposited with the Cambridge Crystallographic Data Centre, CCDC 222272.

2.3. $1,1'$ -(1-Propene-1,3-diyl)-ferrocene (**3a**)

A solution of **2a** [24] (1.2 g, 3 mmol) in dry THF (50 ml) was heated to 60°C . To this solution was added dropwise a solution of lithium di-*iso*-propylamide (1 g, 9 mmol) in dry THF (20 ml). Emission of a gas was observed and the solution gradually turned to brown. The reaction was stirred at reflux temperature for 4 hours and then cooled to room temperature. Volatiles were removed under reduced pressure and the remaining solid was extracted with diethyl ether ($3 \times 100 \text{ ml}$). The combined ether extracts were washed with water ($2 \times 150 \text{ ml}$) and then with saturated NaCl(aq) ($1 \times 100 \text{ ml}$, dried over MgSO_4 , and then evaporated under reduced pressure. Finally, the product was purified by column chromatography on silica gel, eluting with hexane, to yield a yellow crystalline solid in variable yield (20–40%). $^1\text{H NMR}$ (benzene- d_6 , 300 MHz) δ 6.10 (dt, $J = 10.5, 2.8 \text{ Hz}$, 1H, CH=), 5.81 (dt, $J = 10.5, 3.9 \text{ Hz}$, 1H, CH=), 4.05 (t, $J = 1.8 \text{ Hz}$, 2H, $\text{C}_5\text{H}_4\text{CH}$), 4.03 (t, $J = 1.8 \text{ Hz}$, 2H, $\text{C}_5\text{H}_4\text{CH}$), 3.97 (t, $J = 1.8 \text{ Hz}$, 2H, $\text{C}_5\text{H}_4\text{CH}$), 3.84 (t, $J = 1.8 \text{ Hz}$, 2H, $\text{C}_5\text{H}_4\text{CH}$), 2.54 (dd, $J = 3.9, 2.8 \text{ Hz}$, 2H, CH_2). $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz) δ 139.5 (CH=), 120.9 (CH=), 85.7 (C_5H_4 quat.), 84.4 (C_5H_4 quat.), 71.2 ($\text{C}_5\text{H}_4\text{CH}$), 70.2 ($\text{C}_5\text{H}_4\text{CH}$), 69.1 ($\text{C}_5\text{H}_4\text{CH}$), 69.0 ($\text{C}_5\text{H}_4\text{CH}$), 24.8 (CH_2). UV–Vis (CH_2Cl_2): $\lambda_{\text{max}}(\epsilon_{\text{max}})$ 448 nm ($245 \text{ M}^{-1} \text{ cm}^{-1}$). EI-MS m/z 224 (M^+). Analysis (%): Found (Calculated); C, 69.61 (69.68); H, 5.42 (5.40).

2.4. $1,1'$ -(1-Propene-1,3-diyl)-ferrocenium trifluoromethanesulfonate ($[\mathbf{3a}]^+[\text{CF}_3\text{SO}_3]^-$)

A solution of AgCF_3SO_3 (47 mg, 0.17 mmol) in dry THF (5 ml) was added dropwise to a solution of **3a** (41 mg, 0.18 mmol) in dry THF (5 ml). The solution rapidly turned deep green, and a fine silver precipitate was observed. The mixture was stirred for an hour and the volatiles were removed under reduced pressure. The

remaining solid was washed with diethyl ether (3×10 ml) and then extracted into dry CH_2Cl_2 (20 ml). After filtration through a bed of Celite, the solution was then layered with dry pentane (100 ml), resulting in the slow precipitation of a green solid (27 mg, 0.12 mmol, 70%). ES-MS: m/z 224 ($[\mathbf{3a}]^+$). UV-Vis (CH_2Cl_2): λ_{max} (ϵ_{max}) 613 nm ($833 \text{ M}^{-1} \text{ cm}^{-1}$). Analysis (%): Found (Calculated); C, 33.91 (33.96); H, 2.57 (2.64); Fe, 12.61 (12.15).

2.5. 1,1'-[1-(*p*-Toluenesulfonyl)hydrazono-3-phenyl-propene-1,3-diyl]-ferrocene (**2b**)

To a solution of the corresponding ketone, **1b** [25] (80 mg, 0.25 mmol) in ethanol (10 ml) was added dropwise *p*-toluene sulphonyl hydrazide (46 mg, 0.25 mmol) in acetic acid (0.5 ml). This mixture was heated to reflux for 2 h and then cooled to room temperature. Volatiles were removed under reduced pressure and the product was dissolved in CH_2Cl_2 (10 ml). This solution was washed with saturated aqueous NaHCO_3 (3×15 ml) and then dried over MgSO_4 . Finally the volatiles were removed under reduced pressure to afford a yellow–orange crystalline material (96.9 mg, 0.20 mmol, 80%). ^1H NMR (CDCl_3 , 300 MHz) δ 7.75 (t, $J = 8.0$ Hz, 2H, Ph *m*-CH), 7.06–7.24 (m, 7H, overlapping peaks, Ph *o*- and *p*-CH and tolyl CH), 4.42 (t, $J = 1.8$ Hz, 1H, $\text{C}_5\text{H}_4\text{CH}$), 4.40 (t, $J = 1.8$ Hz, 1H, $\text{C}_5\text{H}_4\text{CH}$), 4.38 (t, $J = 1.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{CH}$), 4.05 (t, $J = 1.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{CH}$), 4.25 (t, $J = 1.8$ Hz, 1H, $\text{C}_5\text{H}_4\text{CH}$), 3.95 (t, $J = 1.8$ Hz, 1H, $\text{C}_5\text{H}_4\text{CH}$), 3.63 (dd, $J = 2.3$ Hz, 12.9 Hz, 1H, CHPh), 3.28 (apparent t, $J = 12.9$ Hz, 1H, CH_2 [*H cis* to CHPh]), 2.95 (dd, $J = 2.3$ Hz, 12.9 Hz, 1H, CH_2 [*H trans* to CHPh]), 2.45 (s, 3H, CH_3). ^{13}C NMR (CDCl_3 , 75 MHz) δ 155.9 (C=N), 143.7 (Ar quat.), 143.1 (Ar quat.), 135.0 (Ar quat.), 129.3 (ArCH), 128.2 (ArCH), 127.7 (ArCH), 126.7 (ArCH), 126.3 (ArCH), 89.9 (C_5H_4 quat.), 72.5 ($\text{C}_5\text{H}_4\text{CH}$), 71.7 (C_5H_4 quat.), 71.2 (C_5H_4 2 \times overlapping CH), 71.0 ($\text{C}_5\text{H}_4\text{CH}$), 70.9 ($\text{C}_5\text{H}_4\text{CH}$), 68.5 ($\text{C}_5\text{H}_4\text{CH}$), 68.3 ($\text{C}_5\text{H}_4\text{CH}$), 67.6 ($\text{C}_5\text{H}_4\text{CH}$), 49.6 (CHPh), 45.5 (CH_2), 21.8 (C H_3). UV-Vis (EtOH) λ_{max} (ϵ_{max}) 442 nm ($515 \text{ M}^{-1} \text{ cm}^{-1}$). ES-MS: m/z 484 (M^+ , 20%), 300 (100%, M^+ -NNHTs). Analysis (%): Found (Calculated); C, 64.14 (64.47); H, 5.04 (4.99); N, 5.74 (5.78); Fe, 11.53 (11.45).

2.6. 1,1'-[3-Phenyl-1-propene-1,3-diyl]-ferrocene (**3b**)

A solution of **2b** (0.15 g, 0.5 mmol) in dry THF (10 ml) was heated to 60 °C. To this solution was added dropwise a solution of lithium di-*iso*-propylamide (0.2 g, 1.8 mmol) in dry THF (5 ml). The reaction was stirred at reflux temperature for 4 h and then cooled to room temperature. Volatiles were removed under reduced pressure and the remaining solid was extracted with diethyl ether (3×20 ml). The combined ether extracts were washed with water (2×25 ml) and then with

aqueous saturated NaCl (1×20 ml), dried over MgSO_4 , and evaporated under reduced pressure. The product was purified by crystallization from hexane to give a yellow solid in 15–25% yield. ^1H NMR (CDCl_3 , 300 MHz) δ 7.75 (d, $J = 8.0$ Hz, 2H, Ph *o*-HCH), 7.00–7.30 (m, overlapping peaks, 3H, Ph *m*- and *p*-H), 6.50 (m, 2H, 2 \times CH=), 4.50 (t, $J = 1.8$ Hz, 1H, $\text{C}_5\text{H}_4\text{CH}$), 4.46 (t, $J = 1.8$ Hz, 1H, $\text{C}_5\text{H}_4\text{CH}$), 4.42 (t, $J = 1.8$ Hz, 1H, $\text{C}_5\text{H}_4\text{CH}$), 4.35 (t, $J = 1.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{CH}$), 4.20 (t, $J = 1.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{CH}$), 4.02 (t, $J = 1.8$ Hz, 1H, $\text{C}_5\text{H}_4\text{CH}$), 2.64 (d, $J = 3.8$ Hz, 1H, CHPh). ^{13}C NMR (CDCl_3 , 75 MHz) δ 129.6 (Ph or CH=), 129.0 (Ph or CH=), 128.5 (Ph or CH=), 127.0 (Ph or CH=), 126.8 (Ph or CH=), 126.0 (Ph or CH=), 71.2 (C_5H_4), 70.5 (C_5H_4), 70.3 (C_5H_4), 70.1 (C_5H_4), 69.8 (C_5H_4), 69.2 (C_5H_4), 68.0 (C_5H_4), 26.0 (CHPh) (some overlap of Cp ^{13}C resonances is assumed). UV-Vis (EtOH) λ_{max} (ϵ_{max}) 444 nm ($255 \text{ M}^{-1} \text{ cm}^{-1}$). Analysis (%): Found (Calculated); C, 75.39 (76.02); H, 5.37 (5.62).

2.7. Polymerization experiments

In a nitrogen-filled Vacuum Atmospheres glove-box, **3a** (25 mg, 0.11 mmol) was loaded into an NMR tube and dissolved in dry benzene- d_6 (0.5 ml). A solution of ROMP initiator [**Ru**] or [**Mo**] (1/10, 1/20 or 1/50 equivalent) in dry benzene- d_6 (0.5 ml) was added rapidly to the solution and shaken. The yellow solution was then heated (up to 60 °C for [**Ru**]; up to 40 °C for [**Mo**]) and the progress of the reaction was monitored by ^1H NMR spectroscopy.

In the case of a [**Mo**]-initiated reaction heated for 40 °C, the reaction was quenched after 3 days by addition of excess benzaldehyde. Volatiles were removed under reduced pressure to give a yellow solid. Soluble material **4a** was extracted into THF (3×1 ml) and evaporated under reduced pressure to give an orange solid in ca. 60% yield. ES-MS m/z 896 (1%, $[\mathbf{3a}]_4^+$), 672 (5%, $[\mathbf{3a}]_3^+$), 594 (1%), 532 (1%), 448 (90%, $[\mathbf{3a}]_2^+$), 429 (1%), 370 (1%), 266 (100%), 224 (45%, $[\mathbf{3a}]^+$), 178 (20%). EI-MS 1120 (3%, $[\mathbf{3a}]_5^+$), 896 (100%, $[\mathbf{3a}]_4^+$), 887 (10%), 672 (64%, $[\mathbf{3a}]_3^+$), 448 (36%, $[\mathbf{3a}]_2^+$), 342 (48%), 224 (93%, $[\mathbf{3a}]^+$), 121 (36%). Analysis (%): Found (Calculated for $[\mathbf{3a}]_n$); C, 68.98 (69.68); H, 5.38 (5.40).

3. Results and discussion

1,1'-[1-Propene-1,3-diyl]-ferrocene, **3a**, has previously been synthesized by several methods. Subjecting the tosyl hydrazone of β -oxo-[3](1,1')ferrocenophane to Bamford–Stevens conditions affords **3a** in 70% yield [26]. The corresponding reaction with the tosyl hydrazone of α -oxo-[3](1,1')ferrocenophane, **2a**, is considerably less efficient, with a reported yield of 22% [24]. However, α -oxo-[3](1,1')ferrocenophane, **1a**, can be obtained readily

from ferrocene in one step by a low-temperature Friedel–Crafts reaction with acryloyl chloride [27], whereas its β isomer is only accessible via a multi-step synthesis [26]. We have found that this conversion of the tosyl hydrazone of α -oxo-[3](1,1')ferrocenophane to **3a** may be accomplished in generally somewhat higher, although variable, yield under Shapiro conditions (i.e. a soluble base in a polar solvent at moderate temperature; Scheme 1) [28,29], than reported under Bamford–Stevens conditions (insoluble base, non-polar solvent, high temperature) [30]. We were also able to extend this reaction to 1,1'-(3-phenyl-1-propene-1,3-diyl)-ferrocene (**3b**) – a phenyl-substituted derivative of **3a**.

3a is oxidised at essentially the same potential as ferrocene. **3a** can be chemically oxidized to green $[\mathbf{3a}]^+[\text{CF}_3\text{SO}_3]^-$ using AgCF_3SO_3 ; the visible absorption spectrum of the salt shows an absorption at 613 nm ($\epsilon_{\text{max}} 830 \text{ M}^{-1} \text{ cm}^{-1}$) in dichloromethane, similar to that of unsubstituted ferrocenium [31].

We obtained single crystals of **3a** suitable for X-ray structure determination from hexane. The molecular structure is shown in Fig. 1; details of the structure determination are given in the experimental details (see above) and in information deposited at the Cambridge Crystallographic Data Centre, CCDC 222272. The structure is somewhat disordered (see Section 2); this principally affects the reliability of parameters concerning the three-carbon bridge. The most prominent feature of the structure, which should be relatively unaffected by the disorder is the ring tilt of 11.3° . This angle is somewhat larger than those observed for other [3](1,1')ferrocenophanes with saturated bridges (8.8– 10.9°) [32–36]; comparable dehydro[3](1,1')ferrocenophanes, 1,1'-(1-ferrocenyl-1-propene-1,3-diyl)-ferrocene and 1,1'-(1,3-diferrocenyl-3-methyl-1-propene-1,3-diyl)-ferrocene, have ring tilts of 12.3° and 12.6° , respectively [39,37,38]. Ring tilts of 7.2° and 11.1° have been reported for two independent molecules of the unsaturated [4]ferrocenophane, 1,1'-(1-methoxybutadiene-1,4-diyl)-ferrocene [40]; values of 21.6° and 23° have been reported for CH_2CH_2 and $\text{CH}=\text{CH}$ bridged [2]ferrocenophanes, respectively [4,11]. The observed ring tilt for **3a** suggests that this species may possess sufficient ring

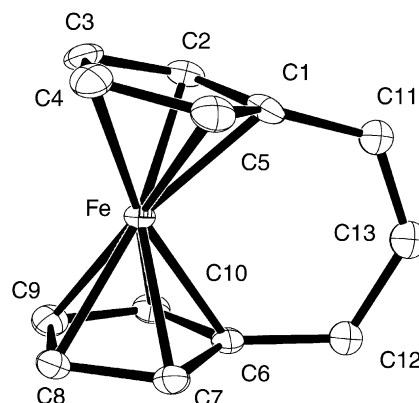
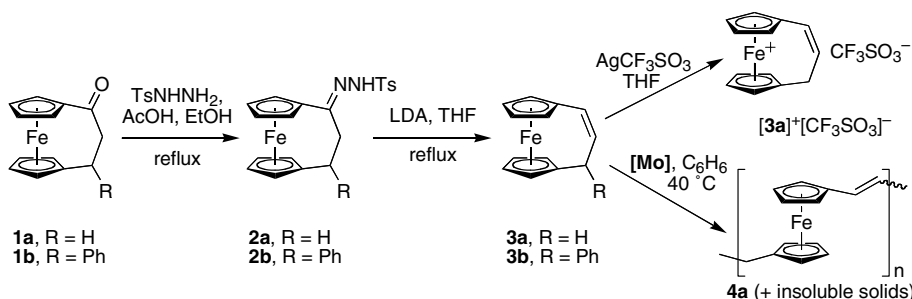


Fig. 1. View of the molecular structure of **3a** with 50% thermal ellipsoids; for clarity, hydrogen atoms are omitted and only one of the two orientations of the disordered bridge is shown. C11–C13 is the $\text{CH}=\text{CH}$ double bond.

strain to be polymerisable using ROMP. As in the structures of many other ring-tilted ferrocenophanes, the $\text{Fe}-\text{C}_{\text{ipso}}$ bonds (2.009(3) and 2.010(3) Å) are significantly shorter than the bonds between iron and the more distant carbon atoms (2.032(3)–2.037(3) Å for carbons adjacent to bridge; 2.059(3) – 2.064(5) Å for the carbons non-adjacent to the bridge).

We have made preliminary investigations of the reaction of **3a** with two commercial ROMP initiators, $\text{Ru}(\text{CHPh})(\text{PCy}_3)_2\text{Cl}_2$ {Cy = cyclohexyl} (**[Ru]**) and $\text{Mo}(\text{CHCMe}_2\text{Ph})[\text{N}(2, 6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)][\text{OCMe}(\text{CF}_3)_2]_2$ (**[Mo]**). Reaction of **3a** with **[Ru]** was monitored by following the disappearance of the initiator carbene peak (20.6 ppm) in the ^1H NMR spectrum; after seven days heating at 60°C in benzene- d_6 , this peak was still present, although diminished in intensity, and, although some new peaks had appeared, peaks attributable to the monomer still remained and indicated that ca. 30% of the **3a** was still present. When **[Mo]** was used in benzene- d_6 , the carbene peak was observed to completely disappear after three days heating at 40°C , and the monomer was essentially totally consumed. Solid material had also appeared in this time. After quenching with benzaldehyde and removal of volatiles, ca. 60% of the residues were found to be soluble in THF. GPC analysis of this soluble material



Scheme 1. Preparation and reactions of dehydro[3](1,1')ferrocenophanes.

(THF vs. polystyrene standards) showed low molecular-weight material ($M_n = 350$; $M_w = 535$; $M_{z+1} = 1484$; PDI = 1.53; it should be noted that the lowest molecular weight standards employed were characterised by $M_p = 580$ and so these values indicated for the molecular weights of the oligomers are only very crude estimates). Interestingly, the main identifiable peaks in both electrospray and electron-impact mass spectra of the soluble fraction correspond to **3a** and its low molecular weight oligomers; although both experiments may be complicated by fragmentations, it is notable that no evidence is found for species of the type shown in Scheme 2(a) and (b), where oligomers have terminal PhCMe₂CH= and PhCH= groups from the initiator and benzaldehyde respectively. Moreover, elemental analysis is consistent with a formulation as [**3a**]_n. Cyclic structures for the oligomers would be consistent with the mass spectra and the analytical data (Scheme 2(c)). Presumably the THF-insoluble fraction consists of higher molecular weight species, either linear or cyclic. Cyclic voltammetry of **4a** shows a single quasi-reversible wave at essentially the same potential as ferrocene; no metal–metal interactions would be expected to be detected given the length of the non-conjugated bridge [41], and similar environments for each ferrocene would be anticipated even though a variety of species are likely to be present.

In summary, we have presented an improved synthesis of dehydro[3](1,1')ferrocenophanes and reported the first crystal structure of a member of this class without bulky substituents. The slow initiation observed in the reactions of **3a** with [Ru] and [Mo] suggests that future attempts to polymerise dehydro[3](1,1')ferrocenophanes should be carried out with a more active catalyst, such as the tungsten species used for the polymerisation of dehydro[4](1,1')ferrocenophanes [12,13]. The formation of insoluble orange material in the present study suggests that poly{dehydro[3](1,1')ferrocenophane} is not highly soluble and therefore suggests that future work should employ derivatives bearing solubilising groups. The

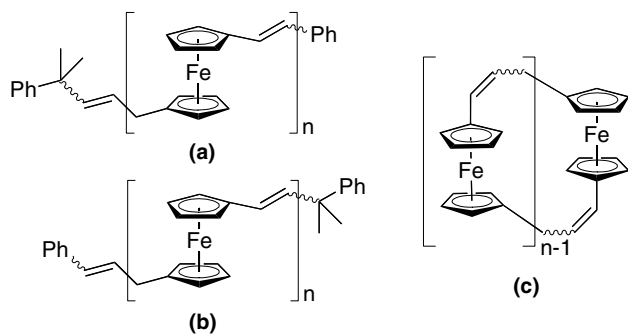
extension of the preparation of **3a** to its phenyl derivative **3b** suggest that such solubilisation could readily be achieved by synthesis of an aryl derivative where the aryl group bears a long alkyl chain. It should also be noted that soluble polymers can potentially be obtained through copolymerisation with other monomers; for example, a block copolymer of norbornene and dehydro(1,1')[2]ferrocenophane was soluble, whereas the homopolymer was insoluble [11].

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References

- [1] P. Nguyen, P. Gómez-Elipé, I. Manners, *Chem. Rev.* 99 (1999) 1515.
- [2] R.D.A. Hudson, *J. Organomet. Chem.* 637–639 (2001) 47.
- [3] I. Manners, *Science* 294 (2001) 1664.
- [4] J.M. Nelson, P. Nguyen, R. Petersen, H. Rengel, P.M. Macdonald, A.J. Lough, I. Manners, N.P. Raju, J.E. Greedan, S. Barlow, D. O'Hare, *Chem. Eur. J.* 3 (1997) 573.
- [5] D.A. Foucher, B.-Z. Tang, I. Manners, *J. Am. Chem. Soc.* 114 (1992) 6246.
- [6] M.T. Nguyen, A.F. Diaz, V.V. Dement'ev, K.H. Pannell, *Chem. Mater.* 5 (1993) 1389.
- [7] R. Rulkens, Y.Z. Ni, I. Manners, *J. Am. Chem. Soc.* 116 (1994) 12121.
- [8] Y. Ni, R. Rulkens, J.K. Pudelski, I. Manners, *Makromol. Chem. Rapid Commun.* 14 (1995) 637.
- [9] N.P. Reddy, H. Yamashita, M. Tanaka, *J. Chem. Soc., Chem. Commun.* (1995) 2263.
- [10] P.F. Brandt, T.B. Rauchfuss, *J. Am. Chem. Soc.* 114 (1992) 1926.
- [11] M.A. Buretea, T.D. Tilley, *Organometallics* 16 (1997) 1507.
- [12] C.E. Stanton, T.R. Lee, R.H. Grubbs, N.S. Lewis, J.K. Pudelski, M.R. Callstrom, M.S. Erickson, M.L. McLaughlin, *Macromolecules* 28 (1995) 8713.
- [13] R.W. Heo, F.B. Somoza, T.R. Lee, *J. Am. Chem. Soc.* 120 (1998) 1621.
- [14] (a) ROMP has also be used to synthesize polymers with pendant ferrocenyl groups D. Albagli, G. Bazan, M.S. Wrighton, R.R. Schrock, *J. Am. Chem. Soc.* 114 (1992) 4150;
(b) K.J. Watson, S.T. Nguyen, C.A. Mirkin, *J. Organomet. Chem.* 606 (2000) 79, and ring-closing olefin metathesis has been used to synthesize 1,1'-(2-butene-1,3-diyl)-ferrocenes;
(c) A.J. Locke, C. Jones, C.J. Richards, *J. Organomet. Chem.* 637–639 (2001) 669;
(d) M. Ogasawara, T. Nagano, T. Hayashi, *J. Am. Chem. Soc.* 124 (2002) 9068.
- [15] W.J. Feast, *Makromol. Chem., Macromol. Symp.* 53 (1992) 317.
- [16] R.H. Grubbs, S.J. Miller, G.C. Fu, *Acc. Chem. Res.* 28 (1995) 446.
- [17] R.R. Schrock, *Top. Organomet. Chem.* 1 (1998) 1.
- [18] R.H. Grubbs, E. Khosravi, *Mater. Sci. Technol.* 20 (1999) 65.
- [19] M.R. Buchmeiser, *Chem. Rev.* 100 (2000) 1565.



Scheme 2. Possible linear (a and b) and cyclic (c) structures for oligo- and poly-**3a**.

- [20] L.M. Tolbert, X. Zhao, Y. Ding, L.A. Bottomley, *J. Am. Chem. Soc.* 117 (1995) 12891.
- [21] S. Barlow, L.M. Henling, M.W. Day, W.P. Schaefer, J.C. Green, T. Hascall, S.R. Marder, *J. Am. Chem. Soc.* 124 (2002) 6285.
- [22] Z. Otwinowski, W. Minor, in: C.W. Carter, R.M. Sweet (Eds.), *Processing of X-ray Diffraction Data Collected in Oscillation Mode*, *Methods Enzymol.*, 276, Academic Press, New York, 1997.
- [23] D.J. Watkin, C.K. Prout, J.R. Carruthers, P.W. Betteridge, *CRYSTALS – Issue 10*, Chemical Crystallography Laboratory, Oxford, UK, 1996.
- [24] M. Applebaum, R.W. Fish, M. Rosenblum, *J. Org. Chem.* 29 (1964) 2452.
- [25] A.J. Locke, C.J. Richards, *Organometallics* 18 (1999).
- [26] A. Sonoda, I. Moritani, *J. Organomet. Chem.* 26 (1971) 133.
- [27] T.D. Turbitt, W.E. Watts, *J. Organomet. Chem.* 46 (1972) 109–117.
- [28] R.H. Shapiro, M.J. Heath, *J. Am. Chem. Soc.* 89 (1967) 5734–5735.
- [29] R.H. Shapiro, M.F. Lipton, K.J. Kolonko, R.L. Buswell, L.A. Capuano, *Tetrahedron Lett.* (1975) 1811–1814.
- [30] W.R. Bamford, T.S. Stevens, *J. Chem. Soc.* (1952) 4735–4740.
- [31] M. Fontani, F. Peters, W. Scherer, W. Wachter, M. Wagner, P. Zanello, *Eur. J. Inorg. Chem.* (1998) 1453.
- [32] S.-J. Jong, J.-M. Fang, *Org. Lett.* 2 (2000) 1947.
- [33] P. Liptau, S. Knüppel, G. Kehr, O. Kataeva, R. Fröhlich, G. Erker, *J. Organomet. Chem.* 637–639 (2001) 621.
- [34] O. Kadkin, C. Näther, W. Friedrichsen, *J. Organomet. Chem.* 649 (2002) 161.
- [35] T.J. Brunker, C. Arisandy, A.R. Cowley, L.H. Rees, S. Barlow, D. O'Hare, *J. Organomet. Chem.* 689 (2004) 252.
- [36] An Fe^{III} species – the TCNQ salt of [3](1,1')ferrocenophane – has a greater ring tilt than **3a** to enable it to accommodate the longer Fe–C bonds found in ferrocenium systems C. Willi, A.H. Reis, E. Gebert, J.S. Miller, *Inorg. Chem.* 20 (1981) 313.
- [37] T.M. Trnka, R.C. Kerber, *Acta Crystallogr. C* 51 (1995) 871.
- [38] C.-F. Chiu, C.-L. Hwang, D.-S. Pan, Y.J. Chen, K.S. Kwan, *J. Organomet. Chem.* 563 (1998) 95–99.
- [39] (a) Structures have also been determined for [3]metallocenophanes in which there are three sp² carbon atoms in the bridge – i.e. a double bond within the bridge, and an exo double bond from the remaining carbon. For example, ring tilts of 12.6°–12.8° have been found for 1,1'-[1-(dialkylamino)butadiene-1,3-diy]ferrocenes S. Knüppel, R. Fröhlich, G. Erker, *J. Organomet. Chem.* 586 (1999) 218;
(b) P. Liptau, S. Knüppel, G. Kehr, O. Kataeva, R. Fröhlich, G. Erker, *J. Organomet. Chem.* 637–639 (2001) 621, and a ring tilt of 9.7° in the 1,1'-[3-(2,4-dihydroxyphenyl)butadiene-1,3-diy]cobaltocenium cation;
(c) P.D. Beer, M.G.B. Drew, D. Heseck, S.M. Lacy, *J. Organomet. Chem.* 511 (1996) 207.
- [40] J.K. Pudelski, M.R. Callstrom, *Organometallics* 13 (1994) 3095.
- [41] S. Barlow, D. O'Hare, *Chem. Rev.* 97 (1997) 637.