The first [2]cobaltocenophane and [2]metallocenophanium salts

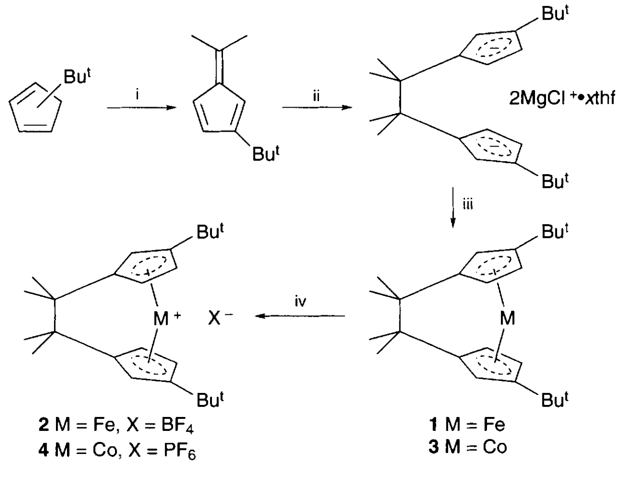
Mark J. Drewitt,[a] Stephen Barlow,[a] Dermot O'Hare,*[a]† James M. Nelson,[b] Paul Nguyen[b] and Ian Manners[b]

[a] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR*
[b] *Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada*

A tetramethylethylene bridged ferrocene 1 and cobaltocene 3 are synthesised in two steps from 2-*tert*-butyl-6,6-dimethylfulvene. Both can be oxidised to the corresponding cations, 2 and 4, the single-crystal X-ray structures of which have been determined.

Strained, ring-tilted [*n*]metallocenophanes have been found to undergo thermal ring-opening polymerisation (TROP).[1–7] The resulting materials are rare examples of well defined, high molecular mass, soluble polymers with transition metals in the main polymer chain. This class of polymers has attracted considerable interest as a result of the unusual physical and chemical properties exhibited.[8] However, metals that have been incorporated into these polymers have been restricted to iron and ruthenium, due to a lack of other strained, ring-tilted metallocenophanes containing any other transition metal. Other main-group [*n*]metallocenophanes with substantial ring tilts have been synthesised, but these have been essentially ionic in nature.[9,10]

We are interested to investigate how the structures and properties of strained [*n*]metallocenophanes varied with electron count, and to see if we could synthesize interesting polymers containing non-iron group metals. Attempts to oxidise [2]ferrocenophane (1,1′-ethylenylferrocene) to its seventeen-electron cation resulted in decomposition and the extremely air-sensitive nineteen-electron 1,1′-ethylenylcobaltocene could only be synthesized in very low yield and identified by its mass spectrum. The metallocenophanes **1** and **3** were prepared as shown in Scheme 1. The ring-substituted anionic tetramethyldicyclopentadienylethane was formed by the reductive coupling of 2-*tert*-butyl-6,6-dimethylfulvene using magnesium/CCl_4 as the reducing agent, this is by an analogous route to that reported by Schwemlein and Brintzinger.[11] Subsequent reaction of this dianion with $FeCl_2·1.5thf$ or $CoBr_2$ in thf afforded **1** and **3** respectively; **1** is a dark orange, air-stable solid, conversely **3** is a dark brown, highly air-sensitive solid, the latter being the first isolated [2]cobaltocenophane. Both **1** and **3** can be conveniently recrystallised from hexamethyldisiloxane. Oxidation of **1** by $AgBF_4$ in thf gave the corresponding salt **2** which is a black, highly air-sensitive solid, this being the first isolated cationic [2]ferrocenophane. Oxidation of **3** by NH_4PF_6 in thf gave the corresponding salt **4** which is a yellow, air-stable solid (both salts are very soluble in polar organic solvents such as CH_2Cl_2 or thf).



Scheme 1 *Reagents and conditions*: i, acetone, pyrrolidine, MeOH, 90%; ii, Mg, CCl_4, thf, 34%; iii, for M = Fe (**1**), $FeCl_2·1.5$ thf, 35%; M = Co (**3**), $CoBr_2$, 25%; iv, for M = Fe, X = BF_4^- (**2**), $AgBF_4$, 80%; M = Co, X = PF_6^- (**4**), NH_4PF_6, 85%; both in thf

Compound **1** was characterized by mass spectrometry.‡ The ^1H and $^{13}C\{^1H\}$ NMR spectra† of **1** indicated the predominance of one isomer; the second isomer was only present in trace amounts which varied from one ligand preparation to another. The cyclic voltammogram of **1** was recorded in dichloromethane and showed a quasi-reversible redox process $E_{1/2}$ at −0.20 V relative to the ferrocenium–ferrocene couple.[12] The EPR spectrum of **2** in a dichloromethane glass at 9 K is characterized by $g_{\parallel}$ = 2.99 and $g_{\perp}$ = 1.94. The *g* aniosotropy ($\Delta g = g_{\parallel} - g_{\perp}$) has been shown to be a valuable probe of the distortion of ferrocenium systems from axial symmetry.[13] The value of Δg = 1.05 for **2** is considerably lower than that found for the 1,1′-trimethyleneferrocenium (*i.e.* [3]ferrocenophanium) cation (Δg = 2.05, 2.19),[14] and approaches that found for other species severely distorted from axial symmetry such as the bis(heptamethylindenyl)iron cation.[15]

Compound **3** was characterized by mass spectrometry† and EPR spectroscopy. The EPR spectrum of a powdered sample of **3** at 7 K is characterized by $g_{\parallel}$ = 2.05 and $g_{\perp}$ = 1.85. These values are similar to those for other cobaltocenes substantially distorted from axial symmetry such as bis(indenyl)cobalt.[16] The cyclic voltammogram of the air-stable cation **4** was recorded in dichloromethane and showed a quasi-reversible redox process $E_{1/2}$ at −1.54 V relative to the ferrocenium–ferrocene couple.[12] The ^1H and $^{13}C\{^1H\}$ NMR spectra‡ of the cation **4** indicated the presence of a single isomer; this was confirmed to be the 3,4′ isomer by single-crystal X-ray crystallography (*vide infra*).

Black single crystals of **2** and yellow single crystals of **4** suitable for an X-ray diffraction study were obtained by layering dichloromethane solutions with diethyl ether.§ A view of the molecular structure of **2** is shown in Fig. 1. The angles α, β and δ used in discussing the structures are defined in Fig. 2. The Fe–C bond lengths [average 2.08(2) Å] in **2** are similar to those in typical ferrocenium ions. Ferrocenium Fe–C bonds are longer than in the corresponding ferrocenes[17] as the HOMO of ferrocene has weak bonding character. Accommodation of these increased bond lengths leads to a very large ring tilt, α, of 29.5°. This is considerably larger than that for 1,1′-(tetramethylethylenyl)ferrocene **5**[18] and 1,1′-(ethylenyl)ferrocene **6**[19] (23 and 21.6° respectively) and very similar to that in 1,1′-(ethylenyl)ruthenocene, (29.6°).[4] The only ferrocene compound with a greater ring tilt is the thia[1]ferrocenophane (31.1°).[20] The eighteen-electron species **4** has typical Co–C bond lengths for a cobaltocenium ion (average 2.03(2) Å, *cf.* 2.04 Å for $[Co(\eta\text{-}C_5Me_5)(tcnq)]$[21]) and a similar ring tilt (24.8°) to those of **5** and **6**. The values of β in **2** and **4** are 8.0 and 9.8° respectively, being similar to that in **5** (9.6°). The degree of distortion can also be appreciated by considering the angle δ which is 160.0° in **2** and

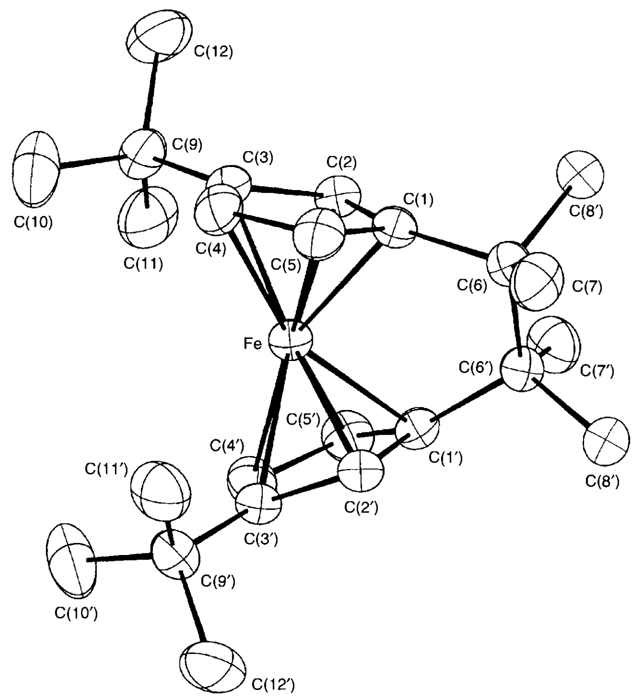


Fig. 1 Molecular structure of **2** (counter ion has been omitted for clarity). Selected interatomic distances (Å): Fe–C(1) 2.008(2), Fe–C(2) 2.056(2), Fe–C(3) 2.157(2), Fe–C(4) 2.139(2), Fe–C(5) 2.044(2), C(6)–C(6′) 1.606(4). Primed atoms are generated by symmetry. Selected interatomic distances (Å) for **4**: Co–C(1) 1.973(2), Co–C(2) 2.025(2), Co–C(3) 2.094(2), Co–C(4) 2.060(2), Co–C(5) 2.012(2), C(6)–C(6′) 1.604(4).

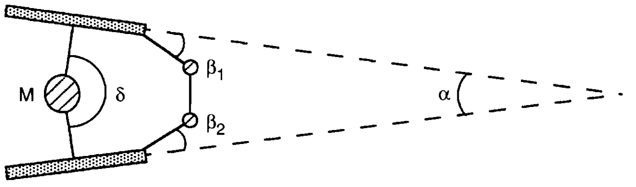


Fig. 2 Definition of structural parameters for [2]metallocenophanes

162.2° in **4** compared to 180° in an ideal unbridged metallocenium ion, and 163.4° in **5**.

The substantial ring tilts observed for **3** and **4** suggested that they may undergo thermal ring-opening polymerisation (TROP). Indeed initial DSC studies on both **3** and **4** indicate that they both exhibit ring-opening exotherms. So far bulk polymerisation reactions have yielded low molecular mass oligomers. However further studies are in progress.

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Footnotes

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‡ *Characterising data* for **1**–**4**. Satisfactory microanalytical data were obtained for compounds **1**–**4** (C, H). All NMR data are recorded at 500 MHz (^{1}H) and 125.7 MHz (^{13}C) and quoted in ppm relative to $\mathrm{SiMe_4}$ (δ 0). For **1**: EIMS, *m/z* 380 ($\mathrm{M^+}$, 100%); NMR data: δ_H ($\mathrm{C_6D_6}$) 1.24 [s, 18 H, $\mathrm{C(CH_3)_3}$], 1.01 [s, 6 H, $\mathrm{C(CH_3)_2}$], 1.23 [s, 6 H, $\mathrm{C(CH_3)_2}$], 3.75 (m, 2 H, CH), 4.43 (m, 2 H, CH), 4.55 (m, 2 H, CH); δ_C ($\mathrm{C_6D_6}$) 27.4 [s, $\mathrm{C}(\mathit{C}\mathrm{H_3})_2$], 28.0 [s, $\mathrm{C}(\mathit{C}\mathrm{H_3})_2$], 30.1 (s, quat.), 32.1 [s, $\mathrm{C}(\mathit{C}\mathrm{H_3})_3$], 48.9 (s, quat.), 66.3 (s, CH), 67.4 (s, CH), 69.4 (s, CH), 95.1 (s, quat.), 103.6 (s, quat.). For **2**: FABMS, *m/z* 380 ($\mathrm{M - BF_4^-}$). For **3**: *m/z* 383 ($\mathrm{M^+}$, 100%). For **4**: FABMS *m/z* 383 ($\mathrm{M - PF_6^-}$); NMR data: δ_H 1.24 [s, 18 H, $\mathrm{C(CH_3)_3}$], 1.37 [s, 6 H, $\mathrm{C(CH_3)_2}$], 1.43 [s, 6 H, $\mathrm{C(CH_3)_2}$], 5.21 (m, 2 H, CH), 5.98 (m, 2 H, CH), 6.11 (m, 2 H, CH); δ_C 27.0 [s, $\mathrm{C}(\mathit{C}\mathrm{H_3})_2$], 27.1 [s, $\mathrm{C}(\mathit{C}\mathrm{H_3})_2$], 30.3 (s, quat.), 31.2 [$\mathrm{C}(\mathit{C}\mathrm{H_3})_3$], 49.6 (s, quat.), 79.8 (s, CH), 81.7 (s, CH), 81.8 (s, CH), 111.5 (s, quat.), 121.4 (s, quat.).

§ *Crystal data*: for **2**, monoclinic, space group *C*2/*c*, a = 12.2090(8), b = 18.5980(9), c = 10.7950(4) Å, β = 103.470(3)°, U = 2383.7(2) $\mathrm{Å^3}$, Z = 4, D_c = 1.30 g $\mathrm{cm^{-3}}$, μ = 6.7 $\mathrm{cm^{-1}}$, crystal size *ca.* 0.16 × 0.22 × 0.81 mm, 11514 total (2370 independent) reflections, R = 0.047, R_w = 0.058 for 1980 reflections with $I > 4\sigma(I)$, max., min. peak in final Fourier difference synthesis 0.48, −0.35 e $\mathrm{Å^{-3}}$ respectively. Room-temp. data were collected on an image-plate Enraf-Nonius DIP 2000 diffractometer using graphite-monochromated Mo-Kα radiation; 90 frames at a step of 2° yielded 11514 reflections, θ_max = 26°.

For **4**: monoclinic, space group *C*2/*c*, a = 11.7040(5), b = 20.032(1), c = 10.8769(8) Å, β = 100.689(5)°, U = 2505.8(5) $\mathrm{Å^3}$, Z = 4, D_c = 1.40 g $\mathrm{cm^{-3}}$, μ = 8.0 $\mathrm{cm^{-1}}$, crystal size *ca.* 0.33 × 0.39 × 0.57 mm, 9030 total (3987 independent) reflections, R = 0.040, R_w = 0.047 for 2673 reflections with $I > 3\sigma(I)$, max., min. peak in final Fourier difference synthesis 0.56, −0.48 e $\mathrm{Å^{-3}}$ respectively. Room-temp. data for the crystal were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation, employing ω–2θ scans (θ_max = 31°). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/206.

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