An Iron Wheel on a Tin Drum: A Novel Assembly of a Hexaferrocene Unit on a Tin–Oxygen Cluster**

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*Dedicated to Professor Herbert W. Roesky
on the occasion of his 65th birthday and to
Professor Samaresh Mitra on the occasion of his 60th birthday*

Multimetallic and multimetallocene assemblies have been attracting attention in recent years for a number of reasons.[1] Recently, the syntheses of a dodecanickel carbosilane dendrimer[2] and a hexametallic cartwheel-type molecule[3] have been reported. These species have been considered as promising materials in homogeneous catalysis because the higher molecular weight multimetallic catalyst can be separated from the reaction medium by nanomembrane filtration.[4] Similarly syntheses of compounds containing a regular arrangement of metallocenes in general and ferrocenes in particular have been pursued with the objective of generating materials possessing useful electric, optical, chemical, and magnetic properties. These include redox-active materials for modification of electrodes[5] or materials which can function as multielectron redox systems[6] or biosensors.[7]

Among the synthetic approaches to prepare macromolecules containing ferrocenes, the most successful strategy has been the ring-opening polymerization of main group element-bridged [1]ferrocenophanes by thermal or anionic methods.[8] Some of these polymers possess interesting electrochemical properties indicative of interaction between iron atoms in the solid state.[9] In contrast to the linear polymers, syntheses of assemblies containing ferrocene units in a cyclic arrangement have been carried out by utilizing various strategies. Astruc and co-workers have pioneered the synthesis of molecular trees where a $[\mathrm{Fe}(\mathrm{C_5Me_5})]$ moiety functions as the core of the tree and the branches can be suitably grafted by alkylation reactions.[10] A heptanuclear complex has been assembled by this approach. Jutzi and co-workers have synthesized decaallylferrocene and have been able to construct dendrimer-like structures.[11] However, both these examples involve multistep synthesis, and X-ray structures of these multiferrocene assemblies have not been reported.

In a radically different approach to the assembly of multiferrocene compounds, we have decided to utilize reactions known in organotin chemistry for this purpose.[12] We report here the preparation of a robust, thermally stable hexaferrocene assembly in quantitative yield by the reaction of two commercially available reactants. The reaction of *n*-butylstannonic acid (**1**) with ferrocene monocarboxylic acid (**2**) in a 1:1 stoichiometry in benzene afforded a dark red compound identified as **3** [Eq. (1); Fc = ferrocenyl].[13] This

$$\underset{\mathbf{1}}{6\,\mathrm{BuSn(O)OH}} + \underset{\mathbf{2}}{6\,\mathrm{FcCOOH}} \xrightarrow[80\,^\circ\mathrm{C}]{\mathrm{C_6H_6}} \underset{\mathbf{3}}{[\{\mathrm{BuSn(O)OC(O)Fc}\}_6]} + 6\,\mathrm{H_2O} \qquad (1)$$

product is obtained in nearly quantitative yield, in contrast to the poor to modest yields usually reported for many multiferrocene compounds. Compound **3**, which contains six ferrocene units, is thermally quite stable and does not undergo any change till 244 °C.

The molecular structure of **3** is shown in Figure 1.[14] The structure shows a giant-wheel arrangement of the six ferrocene units with a drum-like stannoxane central core serving as the structural support for the hexaferrocene assembly. This represents a structural arrangement distinct and unique from the ones observed by others. Most of the nonpolymer ferrocene assemblies involve the linkage of ferrocene units in the form of branches that emanate from a central tree or a core. Unlike these examples, in the present case there is a distinct cyclic connectivity of the six ferrocene units established through the linking tin atoms (Figure 2). In this respect compound **3** is reminiscent of the recently described assembly containing seven ferrocene units doubly bridged to each other by silyl bridges.[15] The structure of **3** shows that the ferrocene carboxylate moiety is involved in binding to two alternate tin atoms of a distannoxane unit. There is a slight asymmetry in

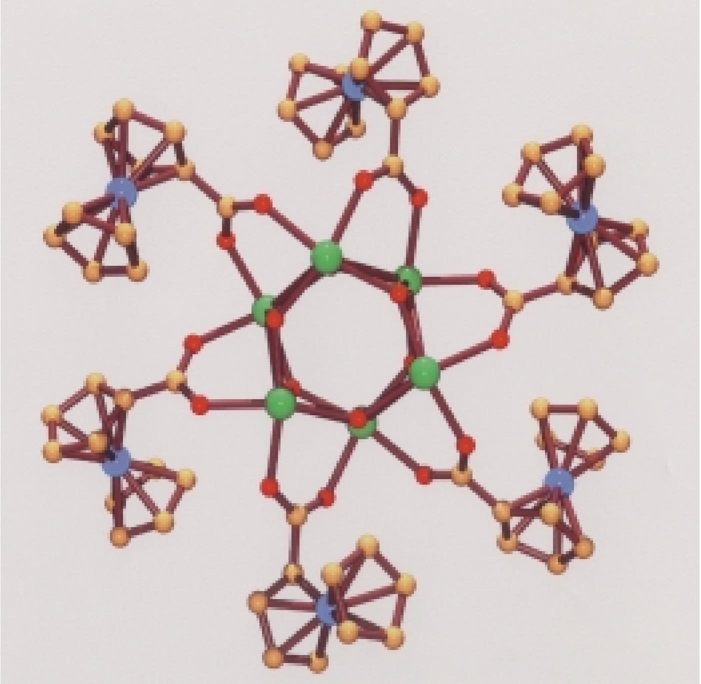

Figure 1. Pov Ray diagram of **3**. The *n*-butyl groups on tin have been omitted for clarity. Red: oxygen, green: tin, yellow: carbon, cyan: iron.

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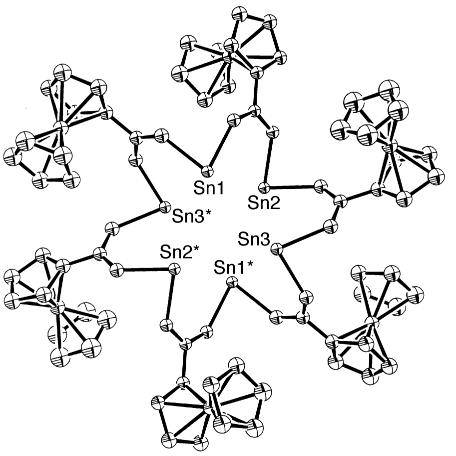

Figure 2. ORTEP diagram of **3** showing the connectivity of the six ferrocene molecules through the tin atoms (the central stannoxane core has been omitted for clarity).

the Sn–O bond lengths arising from the carboxylate linkage (Figure 3). However, the two C–O distances within a ferrocene carboxylate moiety are exactly similar. The central stannoxane cluster in **3** is made up of two hexameric Sn_3O_3 rings, each present in a puckered chair-like conformation. These rings are joined to each other to afford six Sn_2O_2 distannoxane units as the side faces of the cluster. This represents the signature structural feature of stannoxane clusters.[12]

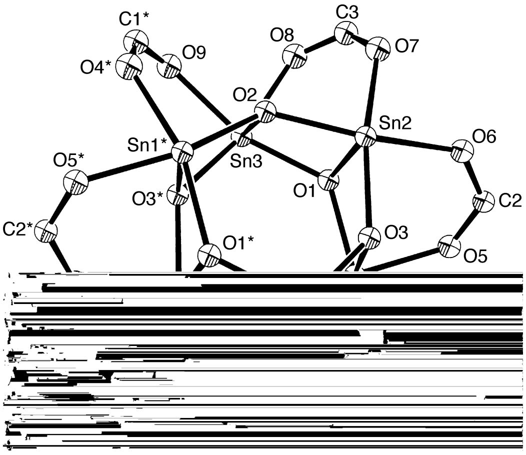

Figure 3. ORTEP diagram of **3** showing the central stannoxane core along with the connecting carboxylate units (the ferrocenyl groups and the *n*-butyl groups have been omitted for clarity). Two crystallographically independent molecules are present in the unit cell. Selected bond lengths [Å] and angles [°] for one of the two molecules: Sn1–O3 2.106(4), Sn1–O1 2.100(4), Sn1–O2* 2.079(3), Sn1–O5 2.142(3), Sn1–O4 2.161(4), C1–O4 1.271(7), C1–O9* 1.270(7); O1-Sn1-O2* 105.20(13), Sn1-O1-Sn3 132.20(17), Sn1-O3-Sn2 100.35(15), O1-Sn1-O3 77.80(14).

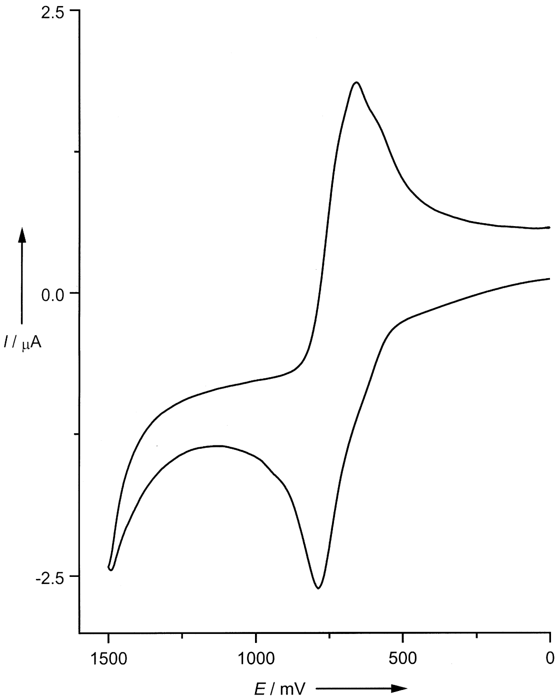

Figure 4. Cyclic voltammogram of **3** at 25 mV s^{-1}. The potential *E* is given versus the saturated calomel electrode (SCE).

Cyclic voltammetric studies on compound **3** show a single quasireversible peak with an $E_{1/2}$ value of 0.73 V (vs. SCE, Figure 4).[16] This suggests that all six ferrocene units are oxidized at the same potential. A comparison of the $E_{1/2}$ values with those of some multiferrocene assemblies is shown in Table 1. A noteworthy feature of the electrochemical behavior of **3** is the reversibility of the voltammogram even after several cycles. Experimentally this has been verified upto ten cycles. This indicates that the cluster is robust and does not decompose upon oxidation. This situation is in contrast to the one reported by Shriver and coworkers, who observed spontaneous decomposition of the ferrocenyl-attached molybdenum cluster $Na_2[Mo_6Cl_8\{O_2C(C_5H_4)Fe(C_5H_5)\}_6]\cdot CH_3OH$ upon oxidation.[17]

Table 1. CV data for **3** and some other multiferrocene derivatives.

Compound	$E_{1/2}$ [V][a]	ΔE_p [mV]	Ref.
$[(C_5H_5)FeC_6\{(CH_2)_5(C_5H_4)Fe(C_5H_5)\}_6]PF_6$	+0.44	55	[10]
$[C_6\{(CH_2)_5(C_5H_4)Fe(C_5H_5)\}_6]$	+0.45	–	[10]
$[(C_5H_5)FeC_6\{(CH_2)_2C_6H_4OC(O)(C_5H_4)Fe(C_5H_5)\}_6]PF_6$	+0.78	60	[18]
$[C_6\{(CH_2)_2C_6H_4OC(O)(C_5H_4)Fe(C_5H_5)\}_6]$	+0.88	120	[18]
$[\{BuSn(O)OC(O)(C_5H_4)Fe(C_5H_5)\}_6]$ (**3**)	+0.72	128	this work

[a] Versus SCE.

Experimental Section

3: A mixture of **1** (0.21 g, 1.0 mmol) and **2** (0.23 g, 1.0 mmol) in benzene (120 mL) was heated under reflux for 6 h using a Dean–Stark apparatus to remove by azeotropic distillation the water formed in the reaction. The reaction mixture was filtered and the solvent removed from the filtrate in vacuo to afford a red-orange powder, which was found to be analytically pure and was shown to be **3**. Diamond-shaped, shining crystals of **3** were obtained in chloroform at 5 °C. Yield: 0.38 g (91.0 %); m.p. 244 °C (decomp.).

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[13] **3**: ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 1.00$ (t, $J = 7.2$ Hz, 3H; CH$_3$), 1.54 (m, 4H; CH$_2$CH$_2$), 1.91 (m, 2H; SnCH$_2$), 4.14 (s, 5H; C$_5$H$_5$), 4.30 (m, 2H; C$_5$H$_4$), 4.82 (m, 2H; C$_5$H$_4$); ^{119}Sn NMR (150 MHz, CDCl$_3$): $\delta = -486.6$ (s).

[14] Crystallographic data for **3** ($C_{90}H_{108}Fe_6O_{18}Sn_6 \cdot 2.57\,CHCl_3$): crystal dimensions $0.51 \times 0.48 \times 0.40$ mm, $M_r = 2831.96$, triclinic, space group $P\bar{1}$; $a = 15.786(8)$, $b = 16.178(8)$, $c = 24.508(12)$ Å, $\alpha = 91.27(2)$, $\beta = 107.328(18)$, $\gamma = 117.499(14)°$; $Z = 2$, $\rho_{calcd} = 1.807$ Mg m^{-3}, $F(000) = 2794$; absorption coefficient 2.480 mm^{-1}. Intensity data were collected using a Bruker SMART ccd area detector[19] mounted on a Bruker P4 goniometer using graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The sample was cooled to 138(2) K. The intensity data, which nominally covered 1.5 hemispheres of reciprocal space, were measured as a series of ϕ oscillation frames, each 0.4° for 30 s per frame. The detector was operated in the 512×512 mode and was positioned 5.00 cm from the sample. Coverage of unique data was 97.9% complete to 25.00° in θ. Cell parameters were determined from a nonlinear least-squares fit of 8192 peaks in the range $3.0 < \theta < 25.0°$. The first 50 frames were repeated at the end of data collection and yielded 698 peaks showing a variation of -0.04% during the data collection. A total of 69782 data were measured in the range $1.50 < \theta < 28.34°$. The data were corrected for absorption by the empirical method[20] giving minimum and maximum transmission factors of 0.296 and 0.353. The data were merged to form a set of 24235 independent data with $R(\text{int}) = 0.0483$. The triclinic space group $P\bar{1}$ was determined by statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2.[21] The hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. A total of 1414 parameters were refined against 776 restraints and 24235 data to give $wR(F^2) = 0.1107$ and $S = 1.080$ for $w = 1/[\sigma^2(F^2) + (0.0364P)^2 + 25.7453P]$, where $P = [F_o^2 + 2F_c^2]/3$. The final $R(F)$ was 0.0431 for the 18440 observed data ($F > 4\sigma(F)$). The largest shift was 0.046 in the final refinement cycle. The final difference map had maxima and minima of 2.122 and -1.415 e Å^{-3}. Three of the *n*-butyl groups are disordered and each is modeled in two orientations. Three solvent sites are found in the regions of the disordered butyl groups, which are also disordered. A fourth disordered solvent site is located away from the main species and is modeled in three orientations. Restraints were applied to the positional and displacement parameters of the disordered atoms. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137558. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[16] Cyclic voltammetric and differential pulse voltammetric studies were performed on a PAR model 273A polarographic analyzer utilizing the three-electrode configuration of a Pt (Beckman) working electrode, a Pt mesh counterelectrode, and a commercially available saturated calomel electrode as the reference electrode interfaced with the computer. Half-wave potentials were measured as the average of the cathodic and the anodic peak potentials. The voltammograms were recorded in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte, and the potential was scanned from -1.5 to $+1.5$ V at scan rates from 25 to 200 mV s^{-1}.

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Molecular Signal Transduction through Conformational Transmission of a Perhydroanthracene Transducer**

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Signal transduction plays an important role in biological systems.[1] While many processes in biological signal transduction[2, 3] use the diffusion of a "second messenger" to the effector site, a molecular transducer linking the receptor and the effector site offers the advantages of a predictable signal distance and signal direction.[4] Herein we show how conformational transmission[5, 6] can be used to design a synthetic transducer.[7] Novel biconformational perhydroanthracene derivatives[8] were synthesized and successfully used as signal transducers in which conformational transmission occurs via a triple ring flip.[9]

Molecular signal transduction via conformational transmission leads, upon a signal stimulus, to a conformational change at the receptor site (Figure 1a). This motion is transmitted by the transducer to the effector site and a second conformational change results in a measurable effect. A good transducer should show a two-state conformational behavior: Binding of the molecular signal should lead to a switching from one conformational state to the other.[10–13] The

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