

Review

# Photoinduced iron–cyclopentadienyl (Fe–Cp) bond cleavage reactions and photocontrolled polymerizations of strained [1]ferrocenophanes

Nga Sze Jeong, Ian Manners\*

*School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, UK*

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## Abstract

Although extensive previous studies have shown that strained [1]ferrocenophanes predominantly undergo ring-opening chemistry at the bridging atom E–cyclopentadienyl (E–Cp) bond, recent reports have highlighted that reactivity at the Fe–Cp bond can also occur, especially on photoactivation. We provide an overview of recent results from our group and those of other researchers. In addition, the development of photocontrolled living polymerizations of sila[1]ferrocenophanes using Fe–Cp bond cleavage chemistry is described. © 2008 Published by Elsevier B.V.

**Keywords:** Photolysis; Ferrocenophane; Insertion reactions; Ring-opening polymerization; Metal-containing polymers

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## 1. Introduction

Since the discovery of the first example, sila[1]ferrocenophane in 1975 by Osborne and co-workers [1], strained [1]ferrocenophanes have attracted considerable attention and have inspired growing interest in a range of related species containing various d- and f-block metals, bridging elements, and even different  $\pi$ -hydrocarbon ligands [2–16]. The angle created by the planes of the two cyclopentadienyl (Cp) rings in a ferrocenophane, generally denoted as  $\alpha$ ,

represents a convenient qualitative measure of the degree of strain present [2]. One of the most important factors that govern  $\alpha$ , and hence the reactivity of [1]ferrocenophanes, is the identity of the bridging atom E. Upon reduction of the covalent radius of the bridging element, [1]ferrocenophanes exhibit increased strain, with larger tilt-angles and an increased bathochromic shift and intensity for the longest wavelength electronic transition [2]. These results have been explained in terms of a decreased HOMO–LUMO gap and, more tentatively, increased ligand character for the LUMO on increasing  $\alpha$  [2,17–19]. The inherent ring-strain in ferrocenophanes also renders these species highly susceptible to ring-opening reactions. For example, sila[1]ferrocenophanes

\* Corresponding author. Tel.: +44 117 928 7650; fax: +44 117 929 0509.  
E-mail address: [ian.manners@bristol.ac.uk](mailto:ian.manners@bristol.ac.uk) (I. Manners).

ring-open upon treatment with a protic source, such as HCl and MeOH, which results in the cleavage of the *ipso*-Cp–Si bond [20,21]. Sila[1]ferrocenophanes also undergo thermal [22], anionic [23] or transition metal catalyzed [24] ring-opening polymerizations (ROP), to give polyferrocenylsilanes (PFS) through cleavage of the *ipso*-Cp–Si bond. When reacted with Pt(0) complexes, sila[1]ferrocenophanes yield platinasila[2]ferrocenophanes by insertion of a Pt fragment into the Si–Cp bond [25].

Although extensive previous studies have shown that [1]ferrocenophanes predominantly undergo ring-opening chemistry at the bridging atom E–Cp bond, recent reports have highlighted that reactivity at the Fe–Cp bond can also occur, especially on photoactivation. This article provides an overview of this emerging area.

## 2. Photoinduced reactions and photocontrolled polymerizations of strained [1]ferrocenophanes

The first [1]ferrocenophane to exhibit iron–cyclopentadienyl (Fe–Cp) bond insertion chemistry was the highly strained boron-bridged analogue (**1**) ( $\alpha \approx 31\text{--}32^\circ$ ) [19]. In the presence of the metal carbonyls  $[\text{Fe}(\text{CO})_5]$ ,  $[\text{Fe}_2(\text{CO})_9]$  or  $[\text{Co}_2(\text{CO})_8]$  and, in the former case, on photoirradiation, bora[1]ferrocenophane underwent Fe–Cp bond insertions to form the dimetallic and trimetallic insertion products **2** and **3**, respectively (Fig. 1).

Also in 2000, Miyoshi and co-workers showed that upon irradiation, phosphorus-bridged [1]ferrocenophanes undergo ring-opening polymerization in THF to give polyferrocenylphosphines [26]. It was proposed that the photolytic polymerization proceeded through the cleavage of the Fe–Cp bond. It was suggested that should photopolymerization occur via Fe–Cp bond dissociation, the vacant coordination site at the Fe centre would be temporarily stabilized by the weakly donating solvent THF which could potentially be displaced by a stronger coordinating ligand. Evidence supporting this novel route was reported

in 2003 when the  $\eta^5$ - to  $\eta^1$ -Cp ring-slipped intermediate **4** was isolated from the photochemical reaction of a phosphorus-bridged [1]ferrocenophane with the P-donor ligand (Scheme 1) [27].

Relevant chemistry was developed before these discoveries for acyclic ferrocene derivatives. In 1998, Kutal and co-workers demonstrated that 1,1'-dibenzoylferrocene can effectively function as photoinitiator in the anionic polymerization of ethyl- $\alpha$ -cyanoacrylate [28]. During the investigation to identify the mechanism for this process, Kutal et al. had also carried out detailed studies on the solution photochemistry of benzoyl-substituted ferrocenes by resonance Raman and UV–Vis spectroscopy as well as electrospray ionization mass spectrometry [29,30]. The analysis led to the following major conclusions. Firstly, it was found that the electronic properties of ferrocene changed considerably upon introduction of an electron-withdrawing benzoyl group to one or both of the Cp rings [31]. While ferrocene shows only a weak absorption band at ca. 440 nm, its benzoyl-substituted analogs exhibit absorptions at longer wavelengths (at ca. 485 nm) with an increase in intensity. This is attributed to the introduction of metal-to-ligand charge transfer (MLCT) character to the low-energy electronic transition. The MLCT contribution is evident when considering the limiting resonance structure which emphasizes a transfer of electron density from the Fe centre to the carbonyl oxygen as depicted in Fig. 2.

The benzoyl groups on the Cp rings also allow the possibility of electron delocalization among the conjugated  $\pi$

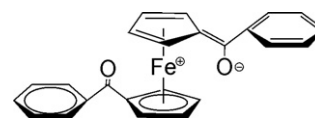


Fig. 2. Limiting resonance structure of MLCT excited state of 1,1'-dibenzoylferrocene.

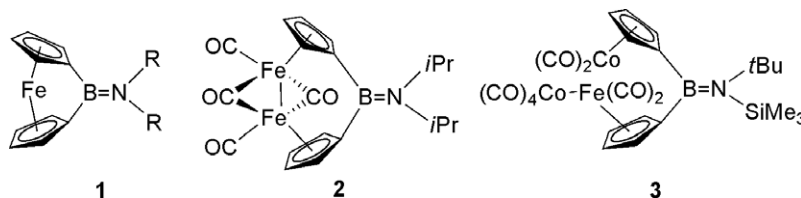
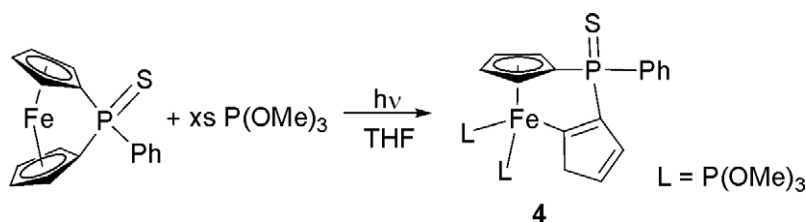


Fig. 1. Structures of **1**, **2** and **3**.



Scheme 1.

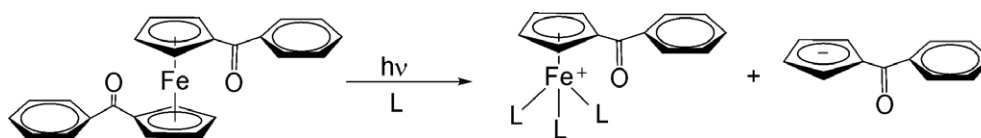
orbitals of the Cp, phenyl and carbonyl groups. This stabilizes the MLCT excited state and therefore a bathochromic shift is observed in 1,1'-dibenzoylferrocene relative to ferrocene. The increase in intensity can be rationalized by an increase in MLCT character which effectively removes the Laporte forbidden character in ferrocene. Based on their work, Kutal and co-workers have also proposed that excitation near the MLCT energy was believed to weaken the Fe–Cp bond by reducing the hapticity of one of the Cp rings from  $\eta^5$  to  $\eta^4$  (Fig. 2) [29–31]. This was also accompanied by an increase in the electrophilicity of the Fe centre and thus facilitated coordination by an incoming ligand such as a weakly donating solvent (L). The analytical data strongly suggested that the photochemical reaction of 1, 1'-dibenzoylferrocene in the presence of a coordinating solvent L led to Fe–Cp bond dissociation, yielding the benzoylcyclopentadienide anion with concomitant formation of the half-sandwich Fe(II) complex stabilized by L (Scheme 2). The former was believed to be the photoinitiator in the anionic polymerization of ethyl- $\alpha$ -cyanoacrylate [29–31].

Inspired by Miyoshi's work on phospho[1]ferrocenophanes and the aforementioned studies regarding 1,1'-dibenzoylferrocene and boron-bridged [1]ferrocenophanes, Tanabe and Manners discovered that under photolytic conditions and in the presence of a mild nucleophilic initiator such as  $\text{Na}[\text{C}_5\text{H}_5]$ , sila[1]ferrocenophane (**6**)

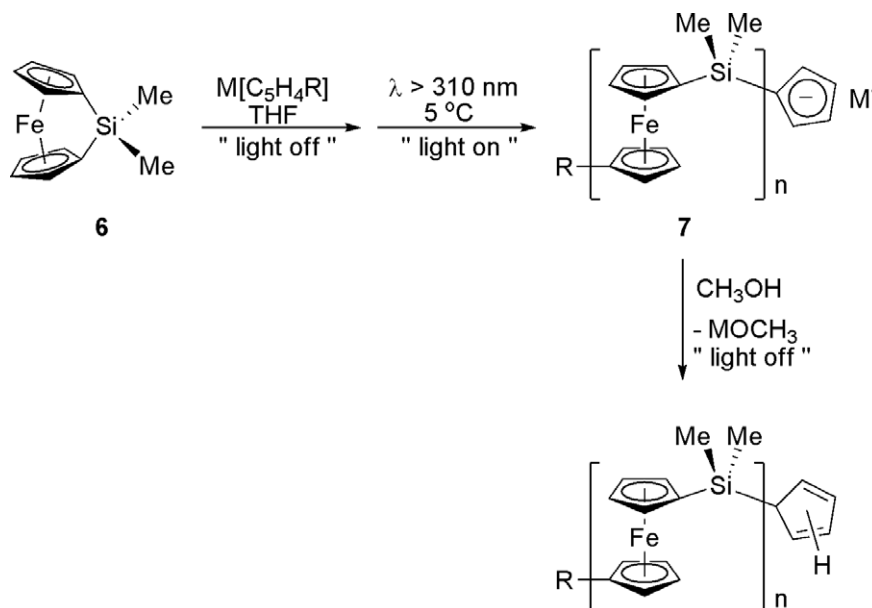
underwent living anionic ROP to give polyferrocenylsilanes with controlled molecular weight and narrow polydispersity (Scheme 3) [32]. The key new concept was to use an initiator ( $[\text{C}_5\text{H}_5]^-$  anion) with improved nucleophilicity, relative to solvent molecule (L), but which, unlike BuLi, has insufficient reactivity to attack the Si centre. The use of the  $[\text{C}_5\text{H}_5]^-$  anion allows efficient initiation and, unlike the case of THF, leads to the formation of stable bonds with the iron centre, thereby ruling out backbiting and macrocondensation reactions which represent statistically random chain termination steps that broaden the molecular weight distribution.

This novel method is fundamentally different from the traditional anionic living ROP of [1]ferrocenophanes which requires a highly basic organolithium reagent as initiator and does not require UV irradiation. Moreover, the new photolytic route involved the unprecedented cleavage of Fe–Cp bond while the conventional anionic living ROP occurs via *ipso*-Cp–Si bond breakage [23]. Significantly, this new polymerization method is milder as the propagating centres are the less basic free silyl-substituted cyclopentadienyl anions **7** instead of the more basic Fe-coordinated Cp anions.

The discovery of this remarkable photocontrolled ROP prompted further studies of the mechanism [33]. Kinetic studies showed that irradiation at wavelength corresponding to the lowest energy absorption of **6** ( $\lambda_{\text{max}} = 480 \text{ nm}$ ) is



Scheme 2.



Scheme 3.

necessary for polymerization to occur in the presence of  $\text{Na}[\text{C}_5\text{H}_5]$  initiator. This has been rationalized as follows. Firstly, theoretical calculations have shown that the increase in the ring-tilt (i.e.  $\alpha$ ) in a [1]ferrocenophane is accompanied by weakening of the Fe–Cp bond and the apparent emergence of the low-lying, ligand-based states [17–19]. Moreover, the aforementioned photochemistry regarding benzoyl-substituted ferrocene indicated that upon photoactivation, 1,1'-dibenzoylferrocene induced a MLCT where an electron is promoted from the bonding d orbital on Fe to the low-lying vacant ligand-based orbital attributed to the carbonyl group. This weakens Fe–Cp bond as well as increases electrophilicity on the Fe centre which is then more prone to attack by a weak donor solvent [29–31]. Thus, it appears likely by analogy that when the strained sila[1]ferrocenophane (**6**) is photoexcited upon irradiation, the weakening of the Fe–Cp bond and the increase in electrophilicity of the Fe centre are expected to favour polymerization in the presence of a weak anionic initiator such as a  $[\text{C}_5\text{H}_5]^-$ .

The kinetics of the photopolymerization were studied at various temperatures (5, 14 and 20 °C) and a living process was proven by the linear plots of  $-\ln(1 - \text{DP}_n[I]_0/[M]_0)$  (where  $\text{DP}_n$  is number-average degree of polymerization, and  $[I]_0$  and  $[M]_0$  are the initial concentrations of initiator and monomer, respectively) versus irradiation time (Fig. 3) [33].

Surprisingly, the slope of this ‘Penczek plot’, which is proportional to propagation rate, decreases with increasing temperature [34]. Moreover, polymerizations at higher temperatures (14 and 20 °C) gave slightly broader molecular-weight distributions (PDI = 1.2–1.3) compared to that

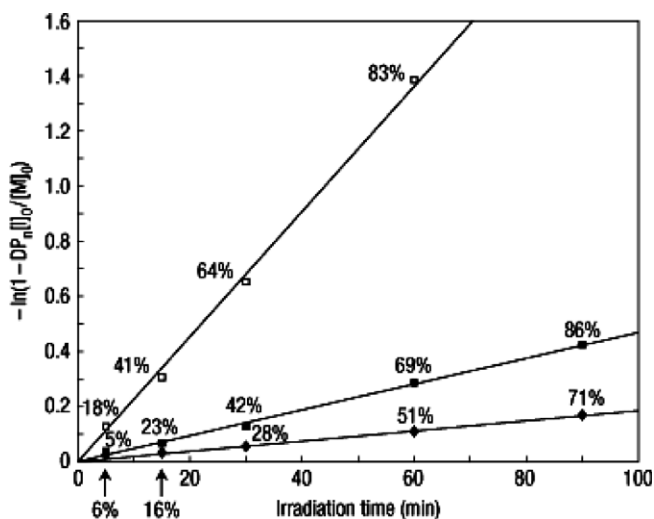


Fig. 3. Plot of  $-\ln(1 - \text{DP}_n[I]_0/[M]_0)$  versus irradiation time for the photopolymerization of **6** using monomer: initiator ratio of 40:1. The percentages at each data point correspond to the respective conversions. Open squares: at 5 °C, filled squares: at 14 °C, filled diamonds: at 20 °C.  $\text{DP}_n$  = degree of polymerization,  $[I]_0$  = initial initiator concentration,  $[M]_0$  = initial monomer concentration. The initial initiator concentration was identical for all three experiments. (Reproduced from Ref. [33] with permission).

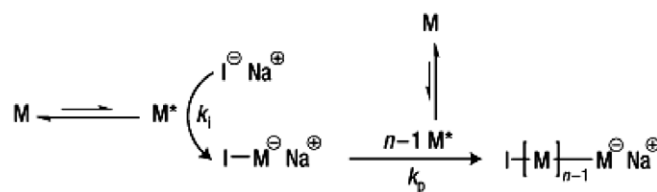


Fig. 4. On irradiation with light, some monomers (M) are promoted to a photoexcited state ( $M^*$ ). The photoexcited monomer  $M^*$  (which is potentially solvated) then reacts with the initiator (I, with rate constant  $k_i$ ) to form a ring-opened monomer, which undergoes chain propagation (with rate constant  $k_p$ ) in the presence of more photoexcited monomer. (Reproduced from Ref. [33] with permission).

at 5 °C (PDI < 1.1). This can be explained by the fact that while photoactivation of the monomer M is independent on temperature, the deactivation of the photoexcited monomer ( $M^*$ ) to regenerate the ground state monomer (M) is more favoured at higher temperatures (Fig. 4) [33]. This leads to slower initiation and polymers with a broader molecular-weight distribution and also a slower rate of propagation. This milder method of photopolymerization is anticipated to permit access to new types of metallopolymers which are otherwise impossible under more basic anionic polymerization using organolithium initiators.

While attempts to polymerize acetylide-functionalized [1]ferrocenophanes by conventional anionic living polymerization initiated by *n*-butyllithium failed due to side reactions with the acetylide substituents, highly metallized block copolymers were successfully prepared through sequential photocontrolled ROP followed by clusterization of the acetylide moieties with metal carbonyls [33]. This

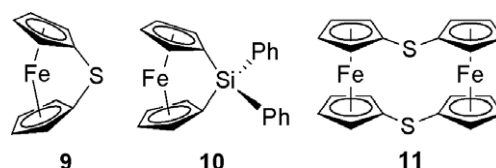


Fig. 5. Structures of **9**, **10** and **11**.

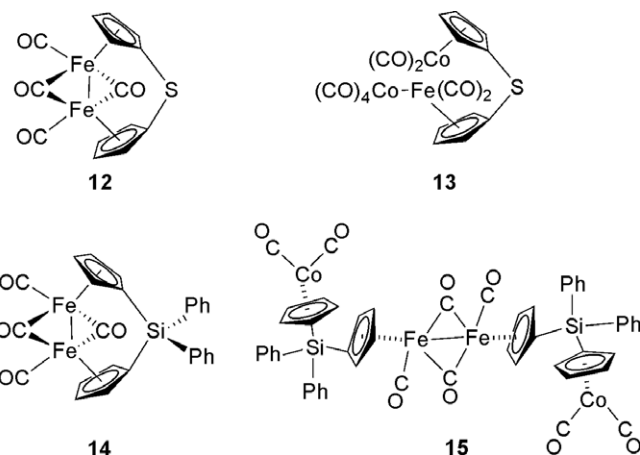
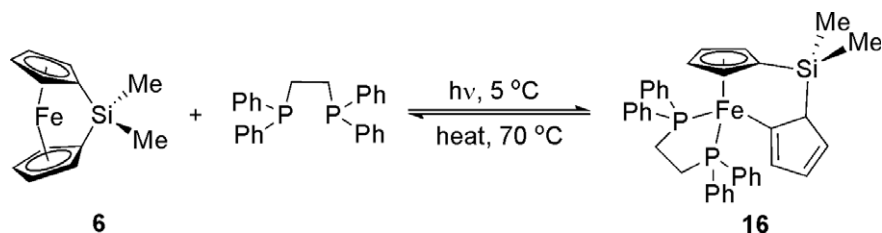


Fig. 6. Structures of **12**, **13**, **14** and **15**.



Scheme 4.

novel polymerization method has the advantage of selectively weakening the Fe–Cp bond and thus allows the use of a milder anionic initiator. This permits the polymerization of monomers which are incompatible with the highly basic initiators and propagating site characteristic of the conventional living anionic method [33].

To date, knowledge about the photolytic reactivity of [1]ferrocenophanes has mainly been confined to the moderately strained **6** and phosphorus-bridged analogs ( $\alpha = 20.8^\circ$ ,  $26.7^\circ$ , respectively) [26,27,32,33]. To gain further insight into the effect of ring-strain on the Fe–Cp bond cleavage, comparative studies have been performed on the photolytic reactivity of the highly strained sulphur-bridged [1]ferrocenophane (**9**) and the moderately strained diphenylsilicon-bridged [1]ferrocenophane (**10**) ( $\alpha = 31.1^\circ$ ,  $19.2^\circ$ , respectively, Fig. 5) in the presence of metal carbonyls ( $[\text{Fe}(\text{CO})_5]$ ,  $[\text{Fe}_2(\text{CO})_9]$  and  $[\text{Co}_2(\text{CO})_8]$ ) [35].

Both **9** and **10** underwent insertion and cleavage reactions at the Fe–Cp bond with relief of ring strain. When irradiated with UV light, the Fe–Cp bond was selectively weakened in both **9** and **10** allowing insertion of metal carbonyl fragments. Significantly, in the case of the highly strained **9**, this selective weakening is sufficient to allow oligomerization in THF and formation of the cyclic dimer **11**, whereas the moderately strained **10** is resistant to this process. It was found that thia[1]ferrocenophane (**9**) underwent faster irradiative and slower non-irradiative insertions with the metal carbonyls ( $[\text{Fe}(\text{CO})_5]$  or  $[\text{Fe}_2(\text{CO})_9]$  and  $[\text{Co}_2(\text{CO})_8]$ ) yielding the respective products **12** and **13** whereas analogous reactions with sila[1]ferrocenophane (**10**) only occurred in the presence of light to form **14** and **15** (Fig. 6).

This was attributed to the greater degree of ring-strain in **9** which possesses an inherently sufficiently weakened Fe–Cp bond. Moreover, the rate of insertion is faster when a stronger coordinating solvent (e.g. THF) is used. This study also suggests that relief of ring strain by cleavage of Fe–Cp bond can potentially be applied to [1]ferrocenophanes with other bridging elements [35].

The discovery of photocontrolled ROP of sila[1]ferrocenophanes has also inspired efforts to isolate the  $\eta^5$ - to  $\eta^1$ -Cp ring-slipped intermediate as has been observed for the phosphorus-bridged analogue [36]. Photochemical reaction of the silicon-bridged [1]ferrocenophane (**6**) in the presence of a bidentate phosphine ligand (1,2-bis(diphenylphosphino)ethane) led to haptotropic shift of a Cp ligand (from

$\eta^5$  to  $\eta^1$ ) to form the corresponding ring-slipped product **16** (Scheme 4).

Interestingly, on heating at  $70^\circ\text{C}$ , the photoproduct **16** underwent dissociation of the phosphine ligand and quantitative retroconversion to the [1]ferrocenophane (**6**). This remarkable phenomenon involving reversible, strain-controlled haptotropic shifts of the Cp ligand was believed to be controlled by a balance between the thermodynamic and kinetic stability of **6** and **16**, respectively [36]. Surprisingly, photolytic ring-opening reaction of sila[1]ferrocenophane in the presence of a bidentate *N*-donor ligand (4,4'-dimethyl-2,2'-bipyridine) did not give the expected ring-slipped photoproduct [37]. Instead a mixture of cyclic oligoferrocenylsilanes and cyclic polymer were formed. In contrast, use of terpyridines led to polyferrocenylsilane formation or the cleavage of both Fe–Cp bonds [38]. Clearly subtle substituent effects play a key role in determining the products that arise from the photoinduced reactivity of the Fe–Cp bonds in ferrocenophanes and fascinating results are also likely for related species [2–16].

### 3. Summary

Photoinduced and photocontrolled Fe–Cp bond cleavage reactions of [1]ferrocenophanes are of intrinsic interest and offer new routes to metallopolymers, which are attracting growing interest as functional materials [39]. Future work in this area is directed towards an investigation of the mechanism of these photolytic reactions of [1]ferrocenophanes with particular emphasis on the nature of the photoexcitation process [31]. Reactivity of the type illustrated in this article may be generally applicable to related strained metallocenophanes and species with other  $\pi$ -hydrocarbon ligands and potentially even unstrained species.

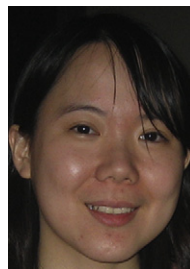
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**Nga Sze Jeong** was born in Hong Kong, China in 1982. She graduated from the University of Toronto in June 2005 with an Honours B.Sc. Degree in Chemistry. In January 2007, she moved to Bristol (England) to start her doctoral studies with Professor Ian Manners investigating the effect of ring strain on the photolytic reactivity of [1]ferrocenophanes as well as developing novel metallopolymers for materials applications.



**Ian Manners** was born in London, England in 1961. After receiving his Ph.D. from the University of Bristol in 1985 in the area of transition metal chemistry (with N.G. Connelly) he conducted postdoctoral work in Germany in main group chemistry (RWTH Aachen, with P. Paetzold), and in the USA on polymeric materials (Penn State, with H.R. Allcock). He joined the University of Toronto, Canada in 1990 and after 15 years returned to his Alma Mater to take up a Chair in Inorganic, Macromolecular and Materials Chemistry, supported by the award of a Marie Curie Chair from the European Union and a Wolfson Research Merit Award from the Royal Society. His research is detailed in over 400 publications and focuses on the development of new synthetic reactions in inorganic chemistry and their applications in molecular synthesis, polymer and materials science, supramolecular chemistry, and nanoscience. Since 2006 he has been a regional editor of *Journal of Organometallic Chemistry*.