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Isolation and characterisation of a well defined precatalyst for the ring-opening polymerisation of silicon-bridged [1]ferrocenophanes

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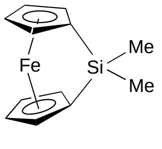
Reaction of the silicon-bridged [1]ferrocenophane $[Fe(\eta\text{-}C_5H_4)_2SiMe_2]$ with $[Pt(cod)_2]$ (cod = cycloocta-1,5-diene) yields a [2]platinasilaferrocenophane $[Fe(\eta\text{-}C_5H_4)_2Pt(cod)SiMe_2]$ which functions as a precatalyst for the ring-opening polymerisation of the silicon-bridged $[Fe(\eta\text{-}C_5H_4)_2SiMe_2]$ to yield the poly(ferrocenylsilane) $[\{Fe(\eta\text{-}C_5H_4)_2SiMe_2\}_n]$; a key step in the mechanism is believed to involve dissociation of the cod ligand.

Transition-metal based polymers such as poly(ferrocenes) represent a growing area of research as a result of their unique physicochemical characteristics and offer potential applications as specialty materials.[1–4] Thermal[5] and anionic[6,7] ring-opening polymerisation (ROP) of strained silicon-bridged [1]ferrocenophanes such as **1** provide excellent routes to high molecular weight poly(ferrocenylsilanes) (*e.g.* **2**) which have attracted recent attention because of their interesting properties.[8–10] This route has been extended to a range of other strained [1]- and [2]-metallocenophanes, and provides access to a series of novel ring-opened organometallic polymeric materials.[8] Desulfurisation-induced ROP of trisulfido-bridged [3]ferrocenophanes has also been reported.[3]

Metal-catalysed ROP of complex **1** using a variety of late-transition-metal complexes containing Pt^{II} (*e.g.* $PtCl_2$), Pt^0 {*e.g.* $[Pt(cod)_2]$ (cod = cycloocta-1,5-diene)}, Pd^{II}, Pd^0 and Rh^I was discovered in 1995, and represents a particularly mild and convenient route to polymers such as **2**.[11,12] By analogy with the proposed mechanism for the transition-metal-catalysed ROP of silacyclobutanes,[13–16] the initial step might be expected to involve insertion of the metal into the strained Si–C bond of **1**, and we have recently reported the first example of this type of reaction in which the [2]platinasilaferrocenophane **3** is formed from **1** and $[Pt(PEt_3)_3]$.[17]

Unfortunately, complex **3** did not act as a catalyst for ROP of **1**, nor did it react with **1** even at elevated temperatures.[17] To more fully probe the mechanism of transition-metal-catalysed ROP of **1** we have reinvestigated the $[Pt(cod)_2]$-catalysed reaction[12] using a high catalyst loading, in the hope of detecting potential intermediates. Thus, a solution containing a 3:1 ratio of **1** and $[Pt(cod)_2]$ was monitored by ^1H NMR spectroscopy over a period of 20 h. This showed an immediate decrease in intensity of the peaks for $[Pt(cod)_2]$ and the appearance of new signals, assigned to cod and a new complex **4**. Polymerisation of **1** was subsequently observed with no changes in intensity of the signals for **4**, the final products being **2**, **4** and cod in an approximate 2:1:1 ratio. Complex **4** was tentatively identified as a [2]platinasilaferrocenophane similar to **3** but with a chelating cod ligand instead of the PEt_3 ligands, and was fully characterised following its controlled synthesis as described below.



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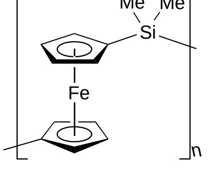

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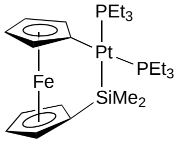

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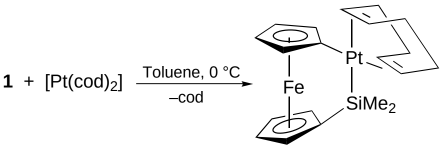
Dropwise addition of *equimolar amounts* of **1** in toluene to $[Pt(cod)_2]$ at 0 °C over 45 min followed by warming to room temperature for 2 h gave **4** and cod [equation (1)].



4

(1)

Orange crystals of complex **4** were isolated in 92% yield from *n*-hexane–toluene at −15 °C and characterised by elemental analysis, mass spectrometry, ^1H, ^{13}C, ^{29}Si and ^{195}Pt NMR spectroscopy.† Both the ^{195}Pt (δ 21) and ^{29}Si (δ −2.83) signals appear as singlets with ^{29}Si satellites ($J_{PtSi} = 1560$ Hz) and ^{195}Pt satellites ($J_{PtSi} = 1563$ Hz), respectively. This coupling constant is greater than that found for the phosphine derivative **3** ($J_{PtSi} = 1312$ Hz)[17] and suggests a stronger Pt–Si bond in **4**. The ^1H and ^{13}C NMR data for **4** are particularly informative and indicate that the olefins of the cod ligand are quite differently bonded to Pt. For example, the $^{13}C\text{-}\{^1H\}$ NMR spectrum has peaks at δ 122.0 ($J_{PtC} = 18$ Hz) and 91.6 ($J_{PtC} = 78$ Hz) respectively assigned to olefinic carbons *trans* to Si and C, consistent with one weakly bound olefin *trans* to the $SiMe_2$ group and one more tightly bound alkene *trans* to carbon. The *ipso* cyclopentadienyl carbon attached to Pt has a ^{13}C NMR resonance at δ 71.7 ($J_{PtC} = 1169$ Hz) indicating a closer Pt–C interaction than in **3** ($J_{PtC} = 850$ Hz).

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† ^1H NMR (400 MHz, C_6D_6): δ 0.60 (m, 6 H, $J_{PtH} = 29$, $SiMe_2$), 1.65 (m, 4 H, cod), 1.82 (m, 4 H, cod), 4.20 (m, 2 H, $J_{PtH} = 31$, $H^{2,5}$), 4.36 (t, 2 H, $H^{7,10}$), 4.52 (t, 2 H, $H^{3,4}$), 4.53 (m, 2 H, $H^{13,14}$), 4.65 (t, 2 H, $H^{8,9}$), 5.38 (m, 2 H, $J_{PtH} = 26$ Hz, $H^{17,18}$); $^{13}C\text{-}\{^1H\}$ NMR (100 MHz, C_6D_6): δ 4.2 (m, $J_{PtC} = 85$, $SiMe_2$), 27.8, 30.8 (cod), 71.0 ($C^{7,10}$), 71.6 (m, $J_{PtC} = 71$, $C^{3,4}$), 71.7 (m, $J_{PtC} = 1169$, C^1), 74.3 (m, $J_{PtC} = 80$, $C^{2,5}$), 75.2 ($C^{8,9}$), 75.8 (m, $J_{PtC} = 74$, C^6), 91.6 (m, $J_{PtC} = 78$, $C^{13,14}$), 122.0 (m, $J_{PtC} = 18$ Hz, $C^{17,18}$); $^{29}Si\text{-}\{^1H\}$ NMR (79.5 MHz, C_6D_6): δ −2.83 ($J_{PtSi} = 1560$ Hz); $^{195}Pt\text{-}\{^1H\}$ NMR (64.2 MHz, C_6D_6): δ 21 (Found: C, 44.50; H, 4.75. Calc. for $C_{20}H_{26}FePtSi$: C, 44.05; H, 4.75%). FAB mass spectrum: $m/z = 545$.

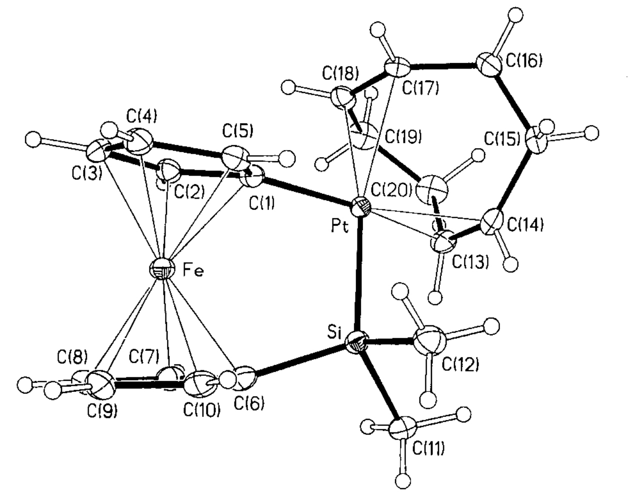

Fig. 1 Molecular structure of complex **4** showing the atom labelling and 30% thermal ellipsoids for all non-hydrogen atoms

The molecular structure of **4** was confirmed by a single-crystal X-ray diffraction study (Fig. 1).‡ As expected, the tilt angle between the cyclopentadienyl ligands is reduced from 20.8(5)° in [1]silaferrocenophane **1** to 10.1(5)° in **4** [*cf.* 11.6(3)° in **3**],[17] and the geometry at the metal centre is essentially square planar [Cp–Pt–Si 86.42(10)°]. Significantly, the Pt–olefin bond distances differ from one another with those *trans* to silicon longer by 0.188(3) Å. In summarising the spectroscopic and structural features of **4**, it is clear that the interaction between Pt and the ferrocenophane moiety is stronger in **4** than in **3**, and that the cod ligand is weakly bonded to the metal, particularly through the olefin *trans* to silicon [C(17)=C(18)].

As for **3**, complex **4** derives from insertion of Pt^0 into the strained H_4C_5–Si bond of **1**. Unlike **3** however, the fact that polymerisation of **1** occurs following formation of **4** from [Pt(cod)$_2$] suggests **4** is either the actual catalyst or a further precatalyst in the [Pt(cod)$_2$]-mediated reactions. A series of experiments have been carried out to determine the role of **4** in the polymerisation of **1**. Thus, when a solution of **1** and **4** (*ca.* 350:1 mol ratio) in C_6D_6 was monitored by ^1H NMR spectroscopy, the resonances for **1** were observed to decrease in intensity accompanied by the appearance of peaks due to polymer **2**. The initially deep red solution turned to amber with a noted increase in viscosity and within 21 h *ca.* 90% conversion to polymer was achieved.§ Gel permeation chromatography (GPC) of the precipitated polymer revealed a monomodal molecular weight distribution with $M_w \approx 2 \times 10^6$, $M_n \approx 1 \times 10^6$.¶ As previously noted the intensities of the ^1H NMR signals of **4** appeared unchanged throughout and no other potential intermediates were observed. This suggests only a small amount of **4** is involved in the polymerisation and is consistent with the high molecular weights observed for **2**.|| Moreover, this implies that **4** is a precatalyst rather than the actual catalytic species.** Interestingly, catalysis using **4** was noticeably quicker than that with [Pt(cod)$_2$], presumably due to inhibition in the latter by cod (see below).

We propose that a key step in ROP of **1** by **4** is the dissociation of the labile cycloocta-1,5-diene ligand forming a co-ordinatively unsaturated [2]platinasilaferrocenophane. Supporting this is the fact that when the reaction is attempted using cod as solvent with a 325:1 mol ratio of **1** to **4** no changes in colour nor viscosity were observed, and monitoring by ^1H NMR revealed no evidence for the formation of polymer even after 7 d.†† The higher than predicted molecular weights of **2** formed *via* Pt-catalysed ROP of **1**, and the relatively unchanged concentration of **4** throughout, suggests that any co-ordinatively unsaturated intermediate is extremely reactive and present in very low concentrations. In other words, very little cod (none could be detected) need dissociate during the reaction for efficient polymerisation to proceed. Other studies on the platinum-catalysed ROP of **1** and sila- or disila-cyclobutanes[14–16] have suggested that chain propagation proceeds either through Pt^0 or Pt^{II} species. The results described herein indicate that the Pt^0 species {[Pt(cod)$_2$]} acts as precursor to a Pt^{II} precatalyst (**4**), although Pt^0-mediated polymerisation cannot be totally ruled out.

In summary, we have shown that [Pt(cod)$_2$] inserts into the strained Si–C bond of [1]silaferrocenophane **1** to give a well defined precatalyst (**4**) that catalyses the ROP of **1** to yield a high molecular weight polymer. We propose that polymerisation proceeds *via* dissociation of the cod ligand in **4** forming a reactive co-ordinatively unsaturated Pt^{II} species. Further detailed investigations into the mechanism of transition-metal-catalysed ROP of [1]silaferrocenophanes and related compounds are underway and will be reported in due course.

Acknowledgements

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‡ An orange crystal of size 0.31 × 0.28 × 0.15 mm was mounted on a Siemens P4 diffractometer equipped with graphite-monochromated Mo-Kα (λ = 0.710 73 Å) radiation. Crystal data for **4**: $C_{20}H_{26}FePtSi$, M = 545.44, monoclinic, space group $P2_1/c$, a = 11.126(3), b = 12.958(4), c = 12.494(3) Å, β = 96.199(9)°, U = 1790.8(8) Å^3, Z = 4, D_c = 2.023 Mg m^{-3}, T = 173(2) K, F(000) = 1056, μ = 8.677 mm^{-1}, maximum and minimum absorption coefficient[18] 0.5389, 0.3591 e Å^{-3}. A total of 5478 reflections were collected in the θ range 2.59–30.03° ($0 \leqslant h \leqslant 15$, $0 \leqslant k \leqslant 18$, $-17 \leqslant l \leqslant 17$), yielding 5237 unique reflections (R_{int} = 0.0219), 5237 of which with $I > 2\sigma(I)$ were considered as observed ($R1$ = 0.0237, $wR2$ = 0.0526). The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL PC.[19] Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/407.

§ The ROP proceeds increasingly slowly at 25 °C because of the decreased convective mixing due to the viscosity increase. Under these conditions (25 °C) complete conversion into **2** takes *ca.* 15–20 d, however, at 65–80 °C quantitative conversion into **2** is observed in 3–4 h.

¶ Comparable values of $M_w = 1.7 \times 10^6$ and $M_n = 6.1 \times 10^5$ have been reported for the [Pt(cod)$_2$] polymerisation of **1**, see ref. 12. The GPC data were recorded in tetrahydrofuran and are relative to polystyrene standards.

|| Given ratios of **1**:**4** of 350:1, if all of **4** is involved in initiation of polymer chains an M_n value ≈8.5 × 10^4 would be expected.

** A species analogous to **4** where Pt has inserted into a silacyclobutane has been tentatively identified as an intermediate during the [Pt(cod)$_2$]-catalysed ROP of a silacyclobutane; see ref. 16.

†† A referee has pointed out that cod might also inhibit the polymerisation of **1** by interfering with radical processes.

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