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FULL PAPER

Insertion of a platinum(0) fragment into the strained silicon–carbon bond of a silicon-bridged [1]ferrocenophane: synthesis, alkyne insertion chemistry, and catalytic reactivity of the [2]platinasilaferrocenophane Fe(η^5-C_5H_4)$_2$Pt(PEt_3)$_2$SiMe$_2$

Karen Temple,[a] **Alan J. Lough,**[a] **John B. Sheridan** *[,b] **and Ian Manners** *[,a]

[a] *Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario M5S 3H6, Canada*

[b] *Department of Chemistry, Rutgers, The State University of New Jersey, University Heights, Newark, NJ 07102, USA*

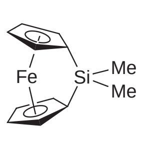
The reaction of Pt(PEt_3)$_3$ with the silicon-bridged [1]ferrocenophane Fe(η^5-C_5H_4)$_2$SiMe$_2$ **1** at 60 °C resulted in the insertion of a platinum(0) Pt(PEt_3)$_2$ fragment into the strained Si–C bond to yield the first [2]platinasilaferrocenophane Fe(η^5-C_5H_4)$_2$Pt(PEt_3)$_2$SiMe$_2$ **4**. Complex **4** serves as a model for the proposed intermediate during the transition metal-catalyzed ring-opening polymerization (ROP) of **1**. The reactivity of **4** was illustrated by the insertion of diphenylacetylene into the Pt–Si bond at elevated temperatures to yield a [4]ferrocenophane Fe(η^5-C_5H_4)$_2$Pt(PEt_3)$_2$C(Ph)C(Ph)SiMe$_2$ **5** with a *cis* Pt–C=C–Si bridge. Both **4** and **5** were fully characterized spectroscopically and by single crystal X-ray diffraction. Despite the reactivity of the Pt–Si bond, the [2]platinasilaferrocenophane **4** was inactive as a ROP catalyst for **1** even at 95 °C. However, addition of BH_3·THF co-catalyst rendered **4** active towards the ROP of **1** at 25 °C, presumably *via* abstraction of one or more PEt_3 ligands, affording low molecular weight [M_n (number average molecular weight) = *ca.* 1720–4695; PDI (polydispersity index) = 1.51–1.73], cyclic poly(ferrocenylsilanes) **6**.

Transition metal-catalyzed polymerizations of organic monomers have been well studied and are of widespread and still growing importance.[1,2] Recently, transition metal-mediated routes to inorganic and organometallic polymer systems have attracted increasing attention. In particular, early transition metal-catalyzed dehydrocoupling reactions have provided attractive routes to σ-conjugated materials such as polysilanes[3] and polystannanes[4] and metal-catalyzed ring-opening polymerization (ROP) of silacyclobutanes has also been well established as a route to high molecular weight polycarbosilanes.[5,6]

We are particularly interested in the synthesis, properties and applications of new classes of polymers with transition elements in the main chain such as poly(ferrocenes).[7–9] The ambient temperature transition metal-catalyzed ROP of silicon-bridged [1]ferrocenophanes **1** has been reported using a variety of Rh^I, Pd^0, Pd^{II}, Pt^0 and Pt^{II} catalysts to yield high molecular weight poly(ferrocenylsilanes) **2** together with, in some cases, the cyclic dimer **3** as a by-product.[10–12] This particularly mild, convenient and versatile route, which has been shown to permit molecular weight and architectural control,[13] complements our previously described thermal[7] and anionic,[14] and recently discovered cationic[15] ROP routes to these interesting materials. The elucidation of the mechanism of these novel transition metal-catalyzed ROP reactions is therefore of considerable interest. By analogy with the tentatively proposed mechanism for the transition metal-catalyzed ROP of silacyclobutanes,[16–19] the initial step might be expected to involve insertion of the transition metal into the strained Si–C bond of **1**. As a follow up to our recent communication,[20] we report in detail our studies of the first example of this type of reaction and our investigation of the reactivity of the resulting [2]platinasilaferrocenophane.

Results and Discussion

Effective catalysts for the ambient temperature ROP of [1]silaferrocenophane **1** range from Pt^{II} and Pd^{II} species such as PtCl$_2$, PdCl$_2$ and Pd(cod)Cl$_2$, to compounds such as Pt(cod)$_2$ involving zero-valent platinum and the Rh^I complex, [Rh(cot)$_2$-(μ-Cl)]$_2$. In contrast, ROP was not observed with a significant number of complexes including [Rh(cod)$_2$(μ-Cl)]$_2$, RhCl(PPh_3)$_3$, and phosphine complexes of platinum and palladium such as Pt(PPh_3)$_3$.[10,11] Interestingly, in the presence of catalytic amounts of Pd(PR_3)$_2$Cl$_2$, (R = Cy or Bu), **1** has been reported to undergo exclusive cyclodimerization at elevated temperatures to afford **3**.[12] Transition metal-catalyzed ROP of mixtures of **1** with other [1]ferrocenophanes[21,22] or sila- and disila-cyclobutanes[23] has also been shown to permit the formation of random copolymers. In addition, we have recently shown that the regiocontrolled metal-catalyzed ROP of unsymmetrically substituted [1]silaferrocenophanes with different cyclopentadienyl ligands such as Fe(η^5-C_5H_4)(η^5-C_5Me_4)SiMe$_2$ is possible,[13] and that the addition of Et$_3$SiH to **1** allows effective molecular weight control. Moreover, the use of polysiloxanes with Si–H groups allows access to novel graft copolymers.[13]



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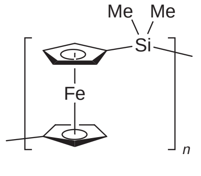

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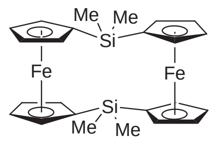


3

A likely first step in the ROP mechanism involves insertion of a transition metal into the strained Si–C bond. Significantly, the strained Si–C bond of [1]silaferrocenophanes appears to mirror the reactivity of strained carbosilacycles which readily polymerize in the presence of Group 9 and 10 metal catalysts and for which the insertion of transition elements to yield metallacarbosilacycles has precedent.[17,24] In efforts to provide evidence for an analogous but unprecedented reaction for [1]silaferrocenophanes we have examined the reactivity of **1** towards low valent late transition metal centres.

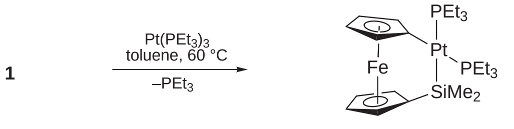
Table 1 Summary of crystal data, details of intensity collection and least-squares refinement parameters

Compound	**4**	**5**
Empirical formula	$C_{24}H_{44}FeP_2PtSi$	$C_{38}H_{54}FeP_2PtSi$
M_r	673.56	851.78
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
T/K	293(2)	293(2)
a/Å	8.2699(14)	10.830(1)
b/Å	19.008(3)	15.807(2)
c/Å	17.719(2)	21.683(2)
β/°	100.565(11)	96.044(7)
U/Å^3	2738.1(7)	3691.1(7)
Z	4	4
μ(Mo-Kα)/cm^{-1}	58.03	43.23
Reflections collected	6575	11 513
R_{int}	0.0387	0.0318
Independent reflections	5959	10 629
No. observed data [$I > 2\sigma(I)$]	4337	6994
$R1[I > 2\sigma(I)]$*	0.0293	0.0365
$wR2(F^2)$*	0.0614	0.0843

* $R1 = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$.

Synthesis and characterization of the [2]platinaferrocenophane, fcPt(PEt$_3$)$_2$SiMe$_2$ 4 (fc = Fe(η^5-C$_5$H$_4$)$_2$)

With prior knowledge that phosphine complexes such as Pt(PPh$_3$)$_3$ do not function as ROP catalysts for **1**, we explored the analogous stoichiometric reaction with the more electron rich Pt^0 complex Pt(PEt$_3$)$_3$, which is known to exhibit a rich range of oxidative-addition chemistry. Addition of equimolar quantities of **1** to toluene solutions of Pt(PEt$_3$)$_3$ followed by heating to 60 °C for 4 h led to a gradual disappearance of **1** as monitored by ^{1}H NMR spectroscopy and formation of the insertion product **4** [equation (1)].



(1)

4

Complex **4** crystallizes from hexane solutions as an air-stable orange crystalline solid and was isolated in *ca.* 80% yield. The new species was characterized using ^{1}H, ^{13}C, ^{31}P, ^{29}Si and ^{195}Pt NMR spectroscopy. Noteworthy is the ^{29}Si NMR resonance at δ 5.18 which shows a large 1312 Hz coupling to Pt as well as couplings of 181 and 14 Hz to phosphorus nuclei of the *trans* and *cis* phosphine ligands respectively. The ^{31}P NMR data show Pt–P couplings of 2160 and 910 Hz, the latter being small due to the strong *trans* influence of the silyl substituent. This is in excellent agreement with the ^{195}Pt NMR spectrum which shows a doublet of doublets, centred at δ −4661.0 with coupling to two inequivalent phosphorus nuclei of 2156 and 915 Hz. The ^{1}H and ^{13}C NMR data are consistent with a [2]platinasilaferrocenophane structure in that four and six cyclopentadienyl (Cp) resonances are observed respectively. Of these, the ^{13}C-{^{1}H} NMR signals for C^1 and C^6 are of particular interest. Thus, C^1 appears as a multiplet centered at δ 73.3 with a large Pt–C coupling of 850 Hz, whereas that for C^6 is a multiplet at δ 84.9 with a much smaller J_{PtC} of 60 Hz. The downfield chemical shifts of C^1 and C^6 are notably different from that of the *ipso* carbons in the highly strained parent [1]silaferrocenophane **1** which appear at δ 33.5.

In order to more fully investigate the novel structure of **4** an X-ray diffraction study was undertaken. Suitable crystals were grown from hexane solution at *ca.* −10 °C over 2 d and a labelled thermal ellipsoid plot of **4** is shown in Fig. 1. An accompanying summary of cell constants and data collection parameters are listed in Table 1.

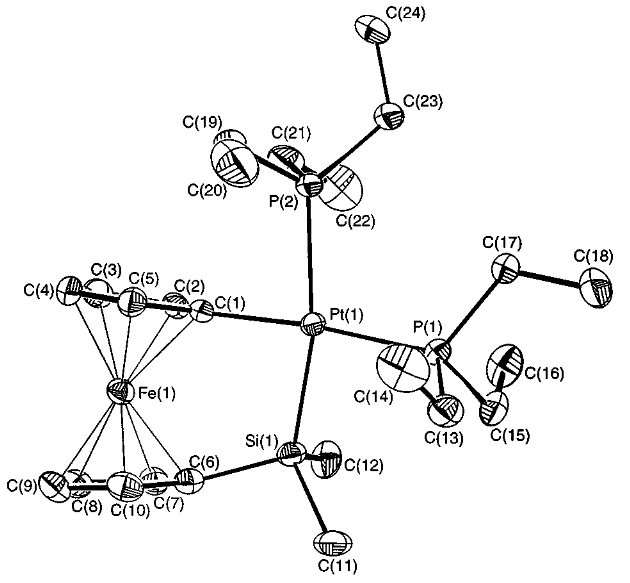


Fig. 1 Molecular structure of **4** shown with 30% thermal ellipsoids

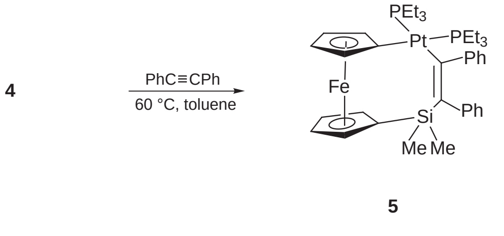
The structure reveals the molecule is slightly strained with a tilt angle of 11.6(3)° between the C$_5$H$_4$ planes, much less than in **1** [20.8(5)°].[8] The platinum centre is in a distorted square planar environment with a larger than expected P–Pt–P angle of 102.74(5)°, and somewhat compressed P–Pt–C(1) and C(1)–Pt–Si angles of 82.48(13) and 83.28(13)°, respectively. Interestingly, the angle β between the plane of the cyclopentadienyl ligand and the C(1)–Pt bond is only 1.2(3)°, whereas the analogous angle for the *ipso* C–Si bond is 12.8(3)°. The Pt–Si bond is also twisted with respect to the C$_5$H$_4$–Fe–C$_5$H$_4$ vector as revealed by a stagger in the C$_5$H$_4$ rings of 7.6(5)°.

The oxidative addition of complex **1** to Pt(PEt$_3$)$_3$ represents the first well characterized example of an insertion of transition metal into the strained Si–C bond of a [1]silaferrocenophane.[20] In order to gain insight into the chemistry of this novel complex, the reactivity and catalytic activity of **4** were probed.

Insertion of diphenylacetylene into the Pt–Si bond of 4: synthesis and characterization of a [4]platinasilaferrocenophane 5

Hydrosilylation[25] and bis(silylation)[26] of unsaturated hydrocarbons, such as acetylenes, in the presence of organometallic catalysts represent well studied reactions. For example, alkynes have been inserted into the Si–C and Si–Si bonds of a variety of species including [2]disilaferrocenophane.[27–29] We therefore attempted the insertion of diphenylacetylene into the Pt–Si bond of **4**.[30]

The direct thermal reaction of **4** and diphenylacetylene in a toluene solution led to the 1,2-insertion of the alkyne into the Pt–Si bond and formation of compound **5** in 38% isolated yield [equation (2)]. Recrystallization of **5** from toluene–*n*-hexanes at −55 °C gave orange, air-stable crystals and characterization by ^{1}H, ^{13}C, ^{31}P and ^{29}Si NMR spectroscopy was consistent with the proposed structure. More specifically, the insertion of diphenylacetylene removes the *trans* influence of the silyl group in **4** increasing one of the Pt–P coupling constants from 910 (for **4**) to 1675 (for **5**) Hz, while the J_{PtP} coupling for the phosphorus



(2)

5

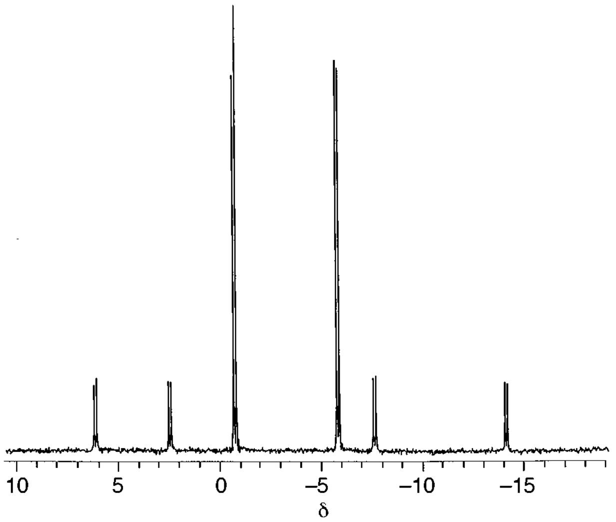


Fig. 2 The ^{31}P NMR (121.5 MHz, C_6D_6) spectrum of complex **5**

trans to the C_5H_4 ligand remains almost relatively constant [*cf.* 2018 Hz (for **5**), 2160 Hz (for **4**) (Fig. 2)]. The ^{13}C NMR spectrum of **5** shows broad resonances at δ 131.5 ($C^{28,32}$) and 127.1 ($C^{29,31}$) assigned to the phenyl group in close proximity to one of the PEt_3 ligands. These broad resonances indicate restricted rotation of this phenyl ring about the C^{25}–C^{27} bond, presumably caused by steric interactions with the PEt_3 group. Both the methyl and methylene resonances of **5** associated with the two PEt_3 groups (δ 8.6 and 17.3, respectively) are consistent with the corresponding peaks assigned in complex **4** (δ 9.0 and 15.9). Interestingly, the two methyl groups of the $SiMe_2$ moiety are separated by 1.0 ppm in the ^1H NMR spectrum. Consideration of the molecular structure reveals the close proximity of one methyl to a phenyl group and hence ring current could contribute to the shift downfield. Unlike **4**, complex **5** shows eight unique signals for the C_5H_4 protons. Likewise, the ^{13}C spectrum displays ten individual resonances for the C_5H_4 carbons with those of the Cp bonded to platinum showing Pt coupling (*cf.* $^1J_{PtC1} = 989$, $^2J_{PtC2,5} = 54$ and $^3J_{PtC3,4} = 77$ Hz). A signal at δ 177.2, typical of metal bound vinyl carbons, with coupling to both ^{195}Pt ($^1J = 863$ Hz) and ^{31}P ($^2J = 112$, 11 Hz) is assigned to C^{25}.

Further confirmation of the structure was obtained by an X-ray diffraction study. Single crystals of **5** suitable for an X-ray diffraction study were grown by cooling a solution of the compound in toluene–*n*-hexanes to −15 °C over 48 h. The molecular structure of **5** is shown in Fig. 3 with an accompanying summary of cell constants and data collection parameters listed in Table 1.

The presence of the sterically encumbering $Pt(PEt_3)_2$ moiety resulted in a number of interesting structural features. In comparison with **4**, the Pt–C(1)–Fe angle [138.4(2)°] is quite obtuse with the C_5H_4 ligand tilting slightly away from the bridging elements. Thus, Pt resides *above* the plane of the ring, causing the angle β to take on a value of −9.8(1)°. This leads to a longer Fe–C(1) bond length 2.145(4) Å and a shorter Fe–C(4) distance of 2.017(5) Å. Steric crowding of the phenyl groups also contracts the Pt–C(25)–C(27) bond angle to 108.3(3)° causing a rather large deviation from the ideal 120°. One phenyl ring is close to the ethyl groups of the phosphine *trans* to C_5H_4 leading to restricted rotation about C(25)–C(27) as evidenced by the ^1H and ^{13}C NMR spectra (see above). The C=C bond length [1.352(5) Å] is somewhat longer than the typical value of 1.317 Å and is only slightly twisted [2.9(1)°] with respect to the C_5–Fe–C_5 centroid axis. Noteworthy is the *cis* orientation of the alkene unit which is consistent with most transition metal-catalyzed alkyne silylation reactions. Undoubtedly, steric crowding of the bulky phenyl groups also plays an important role in the resulting conformation. However, the *cis* stereochemistry of silylation products is consistent with co-ordination of the alkyne prior to migratory insertion *via* the Pt centre.

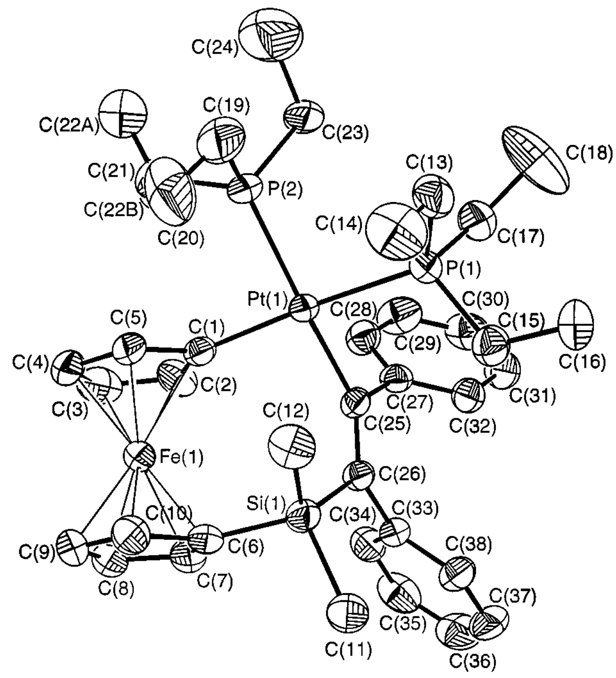


Fig. 3 Molecular structure of **5** shown with 30% thermal ellipsoids

Catalytic activity of the [2]platinaferrocenophane 4 for the ROP of 1 in the absence and presence of BH_3·THF as a co-catalyst

As mentioned above, it is likely that the initial step in the platinum-catalyzed ROP of **1** involves insertion of a Pt^{II} or Pt^0 atom into one of the fc *ipso* C–Si bonds of the ferrocenophane.[16–19] The formation of complex **4** represents the first direct evidence that such a step can occur. However, on addition of *ca.* 1 mol % of **4** to a room temperature toluene solution of **1** no polymerization nor dimerization was detected by NMR spectroscopy. Moreover, polymerization attempts under similar experimental conditions but at an elevated temperature of 95 °C, also proved unsuccessful. The lack of catalytic activity for **4** is consistent with the fact that phosphine derivatives of the Group 9 and 10 metals do not polymerize [1]ferrocenophanes. This contrasts with the active catalysts that have weakly co-ordinated ligands which allow further addition of ferrocenophane substrate to species akin to **4** leading to the high molecular weight organometallic polymers.[10,11,31] Recent experiments involving an analogous complex of **4** but with a more labile cod ligand generated an effective catalyst for the ROP of **1**.[31] However, in the presence of neat cod, all catalytic activity was arrested. This indicates that the displacement of the co-ordinating ligands to generate a reactive unsaturated platinum centre is necessary prior to polymerization.[31]

Therefore, in the case of **4** where the strongly co-ordinating phosphine ligands prevent catalytic activity, an alternative strategy to the transition metal-catalyzed ROP of **1** involves the abstraction of the phosphines by a strong Lewis acid. Thus, 2 mol % of BH_3·THF was injected into a dichloromethane or THF solution containing an excess of **1** along with 1 mol % of **4** as the catalyst. The polymerization was observed to proceed smoothly with time over a period of 1.5 d reaching 100% conversion as monitored by ^1H NMR spectroscopy. The polymer solution was concentrated and precipitated into *n*-hexanes yielding an orange-red polymer.

The ROP of **1** by **4** proceeds in the presence of both 1 and 2 mol % of BH_3·THF; however, the latter resulted in a qualitatively faster rate of polymerization. The complete absence of

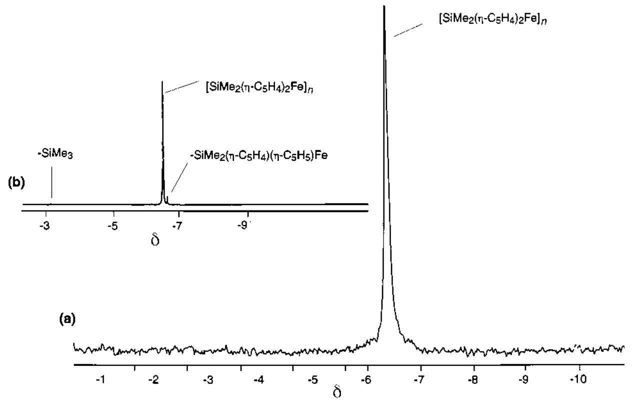
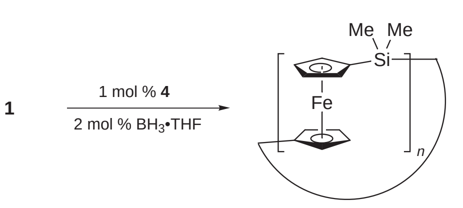


Fig. 4 (a) The ^{29}Si NMR (79.5 MHz, C_6D_6) spectrum of poly(ferrocenylsilane) **6** ($M_n = 4700$, PDI = 1.72) synthesized using catalytic amounts of **4** and BH_3·THF. No resonances were detected in the range δ −200 to 200. (b) The ^{29}Si NMR (79.5 MHz, C_6D_6) of a trimethylsilyl-capped poly(ferrocenylsilane) ($M_n = 8000$, PDI = 1.02) synthesized using living anionic ROP initiated by fcLi and subsequently quenched by Me_3SiCl

any polymerization in a control experiment involving BH_3·THF and **1** confirmed the inability of BH_3·THF alone to initiate the ROP of **1**. Despite a 2 : 1 ratio of BH_3·THF to **4**, not all of **4** is consumed as significant amounts are detectable by ^{31}P NMR spectroscopy even at maximum conversion of **1**. However, the ability of borane to abstract the phosphine ligands of **4** was proven by the appearance of a four line ^{31}P NMR resonance centred at δ 21.4 ($J_{BP} = 59$ Hz) attributed to the formation of the H_3B·PEt_3 adduct.

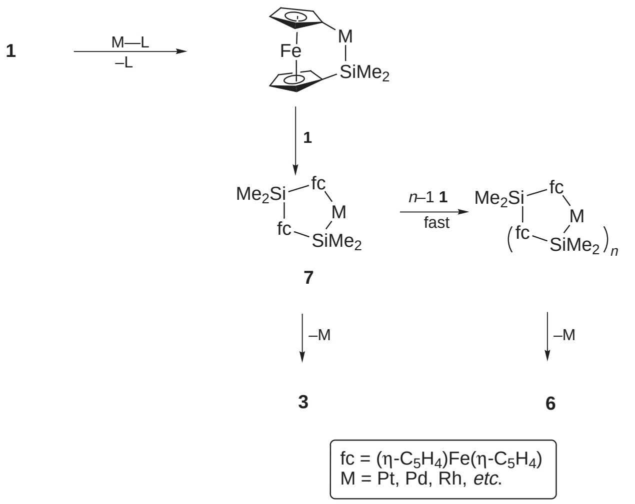
In contrast to other transition metal-catalyzed polymerizations of **1** which yield high molecular weight polymers **2** ($M_w = 10^5$–10^6, $M_n > 10^5$), GPC (gel-permeation chromatography) analyses of the poly(ferrocenylsilanes) using the two component **4**–BH_3·THF catalyst indicated the formation of low molecular weight polymer with M_n (number average molecular weight) = 1720–4695, PDI (polydispersity index) = 1.51–1.73. However, partial oxidation of poly(ferrocenes) can cause artificially low molecular weights to be observed by GPC in THF due to the associated decrease in hydrodynamic radius.[32] We therefore considered it important to verify that the poly(ferrocenylsilanes) formed using the **4**–BH_3·THF catalyst system were indeed in their neutral form. Upon reduction of the product with sodium dihydronaphthylide, no significant apparent increases in molecular weight were observed which indicated that the materials are indeed of low molecular weight. Silicon-29 NMR spectroscopy was utilized to probe the structure of these oligomers which are formed during the phosphine-abstraction route. Interestingly, the ^{29}Si NMR spectra revealed a single resonance at δ −6.4 assigned to $SiMe_2$ units in the interior of the polymer chain [Fig. 4(a)]. However, the spectrum showed no signals that could be assigned to end groups which normally accompany low molecular weight linear poly(ferrocenylsilanes) with $M_n < 8000$.[33] This indicated the important result that the materials have a cyclic structure [**6**, equation (3)].



(3)

6

For comparison, Fig. 4(b) illustrates the corresponding spectrum for linear **2** ($M_n = 8000$, PDI = 1.02) generated by living anionic ROP using fcLi as an initiator followed by quenching with Me_3SiCl. Detectable fc$SiMe_2$ end groups appear slightly upfield of the interior silicon resonances at δ −6.6.



Scheme 1 A mechanism for the transition metal-catalyzed ring-opening polymerization of [1]silaferrocenophanes

These results lend support to the tentative mechanism proposed by us[34] (Scheme 1) which is analogous to that postulated by Tanaka and co-workers for the Pt^0-catalyzed ROP of silacyclobutanes.[24,35] This involves sequential addition of monomer to the metal centre followed by reductive elimination to yield a macrocyclic poly(ferrocene). Reductive elimination from **7** would yield the cyclic dimer, **3**, which is an observed by-product in transition metal-catalyzed ROP reactions in dilute solution.

Conclusion

Insertion of a platinum fragment into the strained Si–C bond has yielded a well defined [2]platinasilaferrocenophane **4** which serves as a model for the proposed key intermediate in the transition metal-catalyzed polymerization of **1**. The ability of this complex to insert diphenylacetylene into the Pt–Si bond provides further evidence for the chemical similarity between the Pt–Si bond of **4** and the Pt–Si bond of platinacarbosilanes.[30] The lack of catalytic activity of **4** towards the ROP of **1** is consistent with the inability of numerous phosphine derivatives of platinum to initiate the transition metal-catalyzed polymerization of **1**. However, in the presence of BH_3·THF co-catalyst, **4** is activated *via* phosphine abstraction to initiate ROP of **1**. In contrast to the high molecular weight polymers typically produced by transition metal-catalyzed ROP,[34] the molecular weights produced by this novel route are invariably low. The absence of end groups in the ^{29}Si NMR of these polymers indicates that the polymer formed is macrocyclic rather than linear. Therefore, the mechanism may involve the generation of a reactive unsaturated platinum center, which might then undergo successive oxidative additions of **1** followed by reductive eliminations of the growing polymer chain to afford macrocyclic poly(ferrocenylsilanes). Further work is currently underway which aims to elucidate the fate of the platinum catalyst and to provide further insight into the catalytic cycles for these interesting ROP processes.

Experimental

Materials

Solvents were dried by standard procedures and distilled immediately prior to use. Diphenylacetylene, PEt_3 and BH_3·THF (1.0 M BH_3 in THF) were purchased from Aldrich and were used as received. [1]Silaferrocenophane **1**[7] and $Pt(PEt_3)_3$ were synthesized as described in the literature.

Equipment

All reactions and manipulations were performed under an inert atmosphere (prepurified N_2) using either standard Schlenk techniques or an inert-atmosphere glovebox (Vacuum Atmospheres), except for the polymers for which manipulations were carried out in air. The reactions and polymerizations were monitored by ^1H and ^{31}P NMR spectroscopy. Solution NMR spectra were recorded on Varian XL 400 instruments. Proton NMR spectra (400 MHz) were referenced to residual protonated solvent and ^{13}C NMR spectra (100.5 MHz) were referenced to the residual protons of the deuteriated solvent. Proton and ^{13}C assignments for **5** were based on an HMQC (Heteronuclear Multiple Quantum Coherence-reverse detection) heteronuclear correlation experiment.[36] Silicon-29 NMR (79.5 MHz) spectra were referenced externally to $SiMe_4$ utilizing a normal (proton decoupled) pulse sequence. For the ^{31}P-{^1H} NMR (121.5 MHz) spectra, H_3PO_4 served as the external reference. Solid-state ^{29}Si NMR was run on a Bruker DSX 400 MHz spectrometer. Molecular weight distributions were analyzed by gel permeation chromatography using a Waters Associates 2690 separations unit. Ultrastyragel columns with a pore between 500, 10^3 and 10^5 Å, and a Waters 410 differential refractometer were used. A flow rate of 1.0 mL min^{-1} was used and samples were dissolved in a THF solution of 0.1% tetra-*n*-butylammonium bromide. Polystyrene standards purchased from Aldrich were used for calibration purposes. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

X-Ray structural characterization

A summary of selected crystallographic data are given in Table 1. Data were collected on a Siemens P4 diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å). The intensities of three standard reflections measured every 97 reflections showed no decay. The data were corrected for Lorentz and polarization effects and a semiempirical absorption correction (calculated from ψ scans) was applied. Minimum and maximum absorption corrections were 0.2548 and 0.3955 for complex **4** and 0.2548 and 0.3955 for complex **5**.

The structures[37] were solved and refined using the SHELXTL PC package. Refinement was by full-matrix least squares on F^2 using all data (negative intensities included). The weighting scheme was $w = 1/\sigma^2(F_o^2) + (0.0186P)^2$ for **4** and $w = 1/\sigma^2(F_o^2) + (0.0371P)^2$ for **5** and where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms were included in calculated positions. Molecular structures are presented with ellipsoids at a 30% probability level for both **4** and **5**.

CCDC reference number 186/1047.

Preparation of $fcPt(PEt_3)_2SiMe_2$ 4

[1]Silaferrocenophane **1** (2.15 g, 8.88 mmol) was added to a toluene solution (10 mL) of $Pt(PEt_3)_3$ (4.83 g, 8.80 mmol), prepared by heating $Pt(PEt_3)_4$ to 60 °C *in vacuo* for 5 h. The deep red solution was heated (60 °C) in an oil bath for 4 h after which time monitoring by ^1H NMR spectroscopy indicated all of **1** had been consumed. The solvent was removed *in vacuo* and the residue extracted with hexanes (20 mL). Cooling to −55 °C overnight gave **4** as orange microcrystals: yield 4.73 g (80%). ^1H NMR (C_6D_6): δ 0.78 (9 H, m, PEt_3), 0.84 (6 H, d, $J_{PtH} = 2.2$, $SiMe_2$), 0.89 (9 H, m, PEt_3), 1.26 (6 H, m, PEt_3), 1.61 (6 H, m, PEt_3), 4.14 (2 H, m, $J_{PtH} = 23.5$ Hz, $H^{2,5}$), 4.40 (2 H, t, $H^{7,10}$), 4.52 (2 H, m, $H^{3,4}$), 4.80 (2 H, t, $H^{8,9}$). ^{13}C-{^1H} NMR (C_6D_6): δ 8.4 (m, $J_{PtC} = 12.5$, PCH_2CH_3, *trans* to silyl group), 9.0 (m, $J_{PtC} = 21.1$, PCH_2CH_3, *cis* to silyl group), 9.1 (m, $J_{PtC} = 84.7$, $J_{PC} = 27.0$, $SiCH_3$), 15.9 (m, $J_{PC} = 16.9$, $J_{PtC} = 10.9$, PCH_2CH_3 *trans* to silyl group), 18.7 (m, $J_{PC} = 27.0$ and 5.1, $J_{PtC} = 28.4$, PCH_2CH_3), 70.0 (s, $C^{7,10}$), 70.5 (m, $J_{PtC} = 52$, $J_{PC} = 15$, $C^{2,5}$), 73.3 (m, $J_{PtC} = 850$, $J_{PC} = 104$ and 14, C^1), 74.3 (m, $J_{PtC} = 65$, $J_{PC} = 4.5$ and 2, $C^{3,4}$), 74.9 (s, $C^{8,9}$), 84.9 (m, $J_{PtC} = 60$, $J_{PC} = 4.5$ and 2 Hz, C^6). ^{31}P-{^1H} NMR (C_6D_6): δ 10.4 (m, $J_{PtP} = 910$, $J_{PP} = 19$, PEt_3 *trans* to silyl group), 11.2 (m, $J_{PtP} = 2160$, $J_{PP} = 19$ Hz, PEt_3 *trans* to C_5H_4). ^{29}Si-{^1H} NMR (C_6D_6): δ 5.18 (m, $J_{PtSi} = 1312$, $J_{PSi} = 181$ and 14.5 Hz). ^{195}Pt-{^1H} NMR (C_6D_6): δ −4661.0 (d of d, $J_{PtP} = 2156$, $J_{PtP} = 915$ Hz) (Found: C, 42.77; H, 6.68. Calc. for $C_{24}H_{44}FeP_2PtSi$: C, 42.80; H, 6.53%).

Preparation of $fcPt(PEt_3)_2(CPh)_2SiMe_2$ 5

A solution of **4** (149 mg, 0.22 mmol) and diphenylacetylene (39 mg, 0.22 mmol) in toluene (3.0 mL) was heated to 60 °C for 24 h after which time the reaction was quantitatively complete as indicated by ^1H NMR spectroscopy. Removal of the solvent *in vacuo* and purification by precipitation from toluene–*n*-hexane solutions at −55 °C gave **5** as an orange crystalline solid: yield 71 mg (38% isolated yield). ^1H NMR (CD_2Cl_2): δ 0.09 (3 H, s, $SiMe_2$), 0.83 (9 H, m, PEt_3), 0.99 (9 H, m, PEt_3), 1.12 (3 H, s, $SiMe_2$), 1.53 (6 H, m, PEt_3), 1.61 (6 H, m, PEt_3), 3.94 (1 H, m, C_5H_4), 3.98 (1 H, m, C_5H_4), 4.01 (1 H, m, C_5H_4), 4.04 (1 H, m, C_5H_4), 4.07 (1 H, m, C_5H_4), 4.09 (1 H, m, C_5H_4), 4.15 (1 H, m, C_5H_4), 4.26 (1 H, m, $J_{PtH} = 25$ Hz, C_5H_4), 6.72 (2 H, t, Ph), 6.82 (2 H, m, Ph), 6.96 (2 H, t, Ph), 7.06 (3 H, br, Ph), 7.20 (1 H, m, Ph). ^{13}C-{^1H} NMR (CD_2Cl_2): δ 2.7 [m, $J_{PtC} = 15$, $Si(CH_3)_2$], 3.5 [s, $Si(CH_3)_2$], 8.6 [m, $J_{PtC} = 15$, $P(CH_2CH_3)_3$], 8.7 [m, $J_{PtC} = 15$, $J_{PC} = 3$ Hz, $P(CH_2CH_3)_3$], 17.2 [m, $J_{PtC} = 25$, $J_{PC} = 20$, $P(CH_2CH_3)_3$ *cis* to C_5H_4], 17.5 [m, $J_{PtC} = 26$, $J_{PC} = 24$, $P(CH_2CH_3)_3$ *cis* to C_5H_4], 66.0 (m, $J_{PtC} = 53$, $J_{PC} = 7$, $J_{PC} = 1$, $C^{2\text{ or }5}$), 66.6 (s, C^6), 67.9 (m, $J_{PtC} = 55$, $J_{PC} = 6$, $C^{2\text{ or }5}$), 69.5 (s, $C^{10\text{ or }7}$), 70.8 (s, $C^{7\text{ or }10}$), 73.8 (s, $C^{9\text{ or }8}$), 74.4 (s, $C^{8\text{ or }9}$), 77.1 (m, $J_{PtC} = 77$, $J_{PC} = 4$, $C^{3\text{ and }4}$, two resonances partially overlapping), 93.6 (m, $J_{PtC} = 989$, $J_{PC} = 118$, $J_{PC} = 11$, C^1), 123.4 (s, C^{30}), 123.8 (s, C^{36}), 126.3 (s, $C^{35,37}$), 127.1 (br, $C^{29.31}$), 131.5 (br, $C^{28,32}$), 131.9 (m, $J_{PtC} = 33$, $J_{PC} = 2$, $C^{34,38}$), 142.0 (m, $J_{PtC} = 43$, $J_{PC} = 6$, $J_{PC} = 3$, C^{27}), 149.3 (m, $J_{PtC} = 86$, $J_{PC} = 12$, $J_{PC} = 2$, C^{26}), 151.2 (m, C^{33}), 177.2 (m, $J_{PtC} = 863$, $J_{PC} = 112$, $J_{PC} = 11$ Hz, C^{25}). ^{31}P-{^1H} NMR (C_6D_6): δ −5.73 ($J_{PtP} = 2018$, $J_{PP} = 16$, PEt_3 *trans* to C_5H_4), −0.65 ($J_{PtP} = 1675$, $J_{PP} = 16$ Hz, PEt_3 *trans* to silyl group). ^{29}Si-{^1H} CP-MAS solid-state NMR: δ 16.3 (Found: C, 53.67; H, 6.33. Calc. for $C_{38}H_{54}FeP_2PtSi$: C, 53.58; H, 6.39%).

Attempted transition metal-catalyzed ROP of 1 by $fcPt(PEt_3)_2SiMe_2$ 4

Complexes **1** (100 mg, 0.41 mmol) and **4** (2.6 mg, 4.1 μmol) were dissolved in C_6D_6, sealed in an NMR tube and heated to 95 °C over a period of 20 h. No polymerization was detected by ^1H NMR spectroscopy.

Transition metal-catalyzed ROP of 1 by $fcPt(PEt_3)_2SiMe_2$ 4 in the presence of $BH_3 \cdot THF$ as co-catalyst

Polymerization: in a typical experiment, complex **1** (532 mg, 2.20 mmol) was dissolved in CH_2Cl_2 (*ca.* 5 mL) after which 1 mol % of **4** (15 mg, 0.02 mmol) and 2 mol % of $BH_3 \cdot THF$ (50 μL, 0.05 mmol) were added. After *ca.* 1.5 d at room temperature, the polymerization was complete as monitored by ^1H NMR spectroscopy. Precipitation of the polymer into *n*-hexanes and drying under vacuum gave 260–348 mg of **6** as an orange solid (50–70%). ^1H NMR (C_6D_6): δ 0.36 (s, $SiMe_2$ of **1**), 3.94 (m, C_5H_4 of **1**), 4.41 (m, Cp of **1**), 0.54 (s, $SiMe_2$ of **6**), 4.09 (m, C_5H_4 of **6**), 4.26 (m, C_5H_4 of **6**). ^{13}C NMR (C_6D_6): δ −0.52 (s, $SiMe_2$ of **6**), 71.97 (s, C_5H_4 of **6**), 72.00 (*ipso* C of C_5H_4 of **6**), 73.82 (C_5H_4 of **6**). ^{29}Si NMR (C_6D_6): δ −6.4 (s, $SiMe_2$ of the interior of **6**). In the ^1H, ^{13}C and ^{29}Si NMR spectra of **6**, no end groups were detectable. In addition, ^{31}P NMR spectroscopy of the polymer did not reveal any phosphorus nuclei after *ca.* 2000 transients. GPC: run 1 (2 mol % $BH_3 \cdot THF$): $M_w = 6330$, $M_n = 3960$, PDI = 1.60; run 2 (2 mol % $BH_3 \cdot THF$): $M_w = 8120$, $M_n = 4695$, PDI = 1.73. Monitoring the polymerization using ^{31}P NMR spectroscopy revealed formation of a $BH_3 \cdot PEt_3$ adduct in addition to a number of unidentifiable by-products. ^{31}P NMR (C_6D_6): δ 21.4 (q, $J_{BP} = 59$ Hz, $Et_3P{\cdot}BH_3$) as identified by comparison with an authentic sample.

Control experiment: complex **1** (75 mg, 0.31 mmol) was dissolved in *ca.* 0.5 mL C_6D_6 and 2 mol % of $BH_3{\cdot}THF$ (0.76 mg, 8.5 μmol) was injected *via* syringe. Monitoring by ^1H NMR spectroscopy at room temperature showed no reaction nor polymerization over a period of 7 d.

Reduction experiment: to a THF (*ca.* 3 mL) solution of polymer **6** (300 mg, 1.24 mmol) was added a solution of $Na[C_{10}H_8]$ in THF (1.0 mL, 1.26 mmol), prepared from the reaction of Na metal (*ca.* 8 g, 0.33 mol) with naphthalene (*ca.* 4 g, 0.03 mol) in the same solvent (25 mL). The resulting solution was precipitated into *n*-hexanes to yield an orange polymer. GPC: run 3 (2 mol % $BH_3{\cdot}THF$): (before reduction) $M_w = 3910$, $M_n = 2590$, PDI = 1.51; (after reduction) $M_w = 5000$, $M_n = 2870$, PDI = 1.74; run 4 (4 mol % $BH_3{\cdot}THF$): (before reduction) $M_w = 2600$, $M_n = 1720$, PDI = 1.51; (after reduction) $M_w = 3360$, $M_n = 2085$, PDI = 1.61. MS (EI, 70 eV) (for run 4): *m/z* 1939 [$M^+ = (fcSiMe_2)_8{}^+$], 1694 [$M^+ - fcSiMe_2$], 1453 [$M^+ - (fcSiMe_2)_2$], 1210 [$M^+ - (fcSiMe_2)_3$], 968 [$M^+ - (fcSiMe_2)_4$], 726 [$M^+ - (fcSiMe_2)_5$], 484 [$M^+ - (fcSiMe_2)_6$], 243 [$M^+ - (fcSiMe_2)_7$].

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