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New Reactivity at the Silicon Bridge in Sila[1]ferrocenophanes

Rebecca A. Musgrave, Rebekah L. N. Hailes, André Schäfer, Andrew D. Russell, Paul J. Gates and Ian Manners*

We describe two new types of reactivity involving silicon-bridged [1]ferrocenophanes. In an attempt to form a [1]ferrocenophane with a bridging silyl cation, the reaction of sila[1]ferrocenophane [Fe(η-C₅H₅)Si(η-C₅H₅)H]₃ (12) (TMP = 2,2,6,6-tetramethylpiperidiny1) towards the hydride-abstraction reagent trityl(triphenylborate) [(C₆H₅)₃C]([C₅F₅H] = 13) (B₅F₅)₃ in low yield. The formation of [13] is proposed to involve abstraction of hydride from the silicon bridge in 12 with subsequent C–H bond cleavage of a cyclopentadienyl group by the resulting electrophilic transient silyl cation intermediate. We also explored the reaction of dimethylsila[1]ferrocenophane [Fe(η-C₅H₅)SiMe₂] (1) with the Au(I) species AuCl(PMe₃)₂. This was found to result in addition of the Au–Cl bond across the C₄P₂—Si bond, to yield the ring-opened species 1[(chlorodimethylsilyl)-ferroceny1](trimethylphosphine)gold(I), [Fe(C₅H₅)Si(η-C₅H₅)Au(PMe₃)] (14). This represents the first example of ring-opening addition of a metalloconophane with a reagent possessing a transition metal-halogen bond.

Introduction

Within a decade of the discovery of ferrocene in the 1950s, the first ansa-metalloccenes, or [n]ferrocenophanes, were prepared. 1,2 [n]Metalloccenes (Figure 1) possess an ansa [n] bridge (an inter-ring bridge composed of n bridging atoms) which links the cyclopentadienyl rings and tilts them about the metal centre. These [n]metalloccenes, combined with analogous species based on other π-hydrocarbon ligands, make up by far the broadest and most well-studied class of strained metal-containing rings, and have attracted substantial attention over the last fifty years. 3-13 Their unusual molecular and electronic structures arise from distortion of the favoured parallel disposition of the Cp rings, resulting in a higher energy (for d²—d⁴ metals), ring-tilted structure.

[n]Ferrocenophanes bridged by a single silicon atom were among the first [n]metalloccenes to be reported, 1,4 and they are at present widely employed as precursors to poly(ferrocenylsilanes) which have attracted much attention as a result of their interesting redox, preceramic, and etch-resistant characteristics and other physical properties. 15-19 [n]Ferrocenophanes are also of interest as ligands, 20, 21 and structural supports for low-valent main group species, with recent examples incorporating carbenes, 22,24 germynes, 25, 26 and stannylenes. 25 Investigation of the reactivity of silicon within [n]ferrocenophanes has led to a good general understanding of the mechanisms for ring-opening and polymerisation processes, and reactivity at the bridging silicon atom in dimethylsila[1]ferrocenophane 1 (Figure 2) is particularly well documented. 27, 28 The polar C₄P₂—Si bond is labile in these strained molecules as a result of various structural distortions, which are visualised by β (the extent to which the coordination environment of the sp³ C₄P₂—Si carbon atom deviates from a trigonal planarity) and θ (an angle which describes the distortion from tetrahedral geometry of the bridging silicon) (see Figure 1).

![Fig. 1 Geometric parameters characterising the structural distortions in the molecular structures of [1]ferrocenophanes. α = dihedral angle between the Cp and Cp' ring planes, β = (180° – (C₄P₂—Si) angle, δ = C₄P₂—Fe–C₄P₂ angle, θ = C₄P₂—Si–Cp' angle.](image)

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Anionic, 28-30 cationic, 31 thermal, 9, 32-35 and transition metal-catalysed ring-opening polymerisation (ROP) 36-38 all proceed via cleavage of this bond, in addition to many stoichiometric ring-opening reactions. 39, 40 To date, most sila[1]ferrocenophanes feature a tetravalent bridging silicon atom which exhibits pseudo-tetrahedral geometry within the ansa bridge. Only two examples of sila[1]ferrocenophanes which feature hypercoordinate silicon atoms have been reported (2 and 3, Figure 2). 31, 41 Coordination of the donor nitrogen- or oxygen-based pendant group in these molecules

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results in lengthening of the trans \( \text{Cp}^{\text{trans}} \)-Si bond, and increases reactivity of this bond towards cationic species.\(^{31}\) No examples currently exist in which the bridging silicon atom exhibits a coordination environment of less than four substituents, despite low coordinate silicon compounds being commonplace in the literature.\(^{42-46}\)

Fig. 2 Tetra-coordinate dimethylsila[1]ferrocenophane 1 and penta-coordinate sila[1]ferrocenophanes 2 and 3.

Silicon cations are very strong Lewis acids and exhibit particularly pronounced electrophilicity: they are commonly termed “super-electrophiles”.\(^{47, 48}\) Only a small number of “true” silylium ions (\( \text{R}_3\text{Si}^+ \)) are considered to have been isolated, where no stabilisation by counter-ions or solvent molecules is evident; namely \((\text{Mes})\text{Si}^+ \),\(^{49-51}\) and related species with bulky aryl substituents.\(^{52-55}\) Unlike in the isoelectronic carbenium ions, where delocalisation of the positive charge is commonplace,\(^{47}\) in silyl ions the charge is predominantly localised at the silicon atom due to the lower tendency for hyperconjugation with the diffuse valence orbitals of silicon,\(^{56}\) resulting in reaction with many weak \( \sigma \)- and \( \pi \)-donor molecules.

Attenuation of this electrophilicity at silicon has been demonstrated by the installation of a ferrocene (Fc) unit.\(^{56-58}\) Effective comparison can be made between the \( \alpha \)-ferrocenyl silyl cation in compound 6 and the isoelectronic borane and carbenium analogues (Figure 3).\(^{59, 60}\)

Fig. 3 Isoelectronic \( \alpha \)-ferrocenylborane 4,\(^{59}\) \( \alpha \)-ferrocenylcarbenium ion 5,\(^{60}\) and \( \alpha \)-ferrocenyl silyl cation 6\(^{56}\) (\( \alpha^\circ = [180^\circ - (\text{Cp}_{\text{trans}}-\text{Cp}^{\text{trans}}-\text{E})] \)) angle).

In all cases, a “dip angle”, \( \alpha^\circ \) (defined as \([180^\circ - (\text{Cp}_{\text{trans}}-\text{Cp}^{\text{trans}}-\text{E})] \)) angle of the electron-deficient \( \alpha \)-substituent towards the iron atom is evident, which increases with the increasing electrophilicity of the substituent from boron to carbon to silicon. The charge in 6 is predominantly localised at silicon, which adopts a quasi-planar configuration, although a Fe–Si bonding interaction is also evident crystallographically. DFT calculations indicated that both the upper and lower Cp rings are involved in bonding with silicon via two 3-centre-2-electron bonds (\( \text{Cp}^{\text{trans}}-\text{Si}-\text{Fe} \) of the upper ring, and \( \text{Fe}-\text{Si}-\text{C} \) of the lower ring), accounting for the particularly large dip angle.\(^{55}\) In this respect, bonding of both Cp rings to Si is reminiscent of \( \text{ansa} \) bridging, characteristic of sila[1]ferrocenophanes.

Scheme 1 Ring-opening protonation of dimethylsila[1]ferrocenophane 1 to yield chlorodimethyl(ferrocenyl)silane 7.

A solvent-stabilised silylium ion was in fact isolated from a sila[1]ferrocenophane precursor in 2000.\(^{63}\) Ring-opening protonolysis of sila[1]ferrocenophanes with HCl has been shown to yield ferroenylchlorosilanes (Scheme 1),\(^{60}\) but the analogous reaction of di(ferrocenyl)sila[1]ferrocenophane (8)\(^{64}\) and HBF\(_4\) yielded a mixture of ferrocenyfluorosilanes, thought to proceed via extraction of \( \text{F}^- \) from \([\text{BF}_4]^–\) by a reactive silicon-based intermediate. Employing ‘Brookhart’s acid’ with weakly coordinating \( [3,5\text{-bis(trifluoromethyl)phenyl}]\text{borate} \) anion (Scheme 2),\(^{65}\) the pyridine-coordinated silyl cation 9 was isolated, exhibiting geometry at silicon intermediate between trigonal planar and tetrahedral.\(^{66}\) No dip angle towards the iron atom is observed in this case as a result of sufficient reduction in electrophilicity at silicon by the pyridine donor ligand.


The syntheses of ferrocene-substituted silylium ions\(^{56-58, 61}\) and \( \text{9}^\circ \) rely on very different methodologies. The first involves hydride abstraction from silicon using the trityl cation (\( [\text{CPh}_3]^+ \)), whereas the second method involves heterolytic cleavage and protonation of a strained C–Si bond. Herein, we intend to apply the hydride abstraction route to a sila[1]ferrocenophane with an Si–H moiety with the intention of synthesising a silylium ion where both \( \text{Cp}^{\text{trans}}-\text{Si} \) bonds remain intact.
Results and Discussion

Using the hydride abstraction route described above, several initial attempts to synthesise silyl cations from monoalkyl-substituted sila[1]ferrocenophanes (such as methylsila[1]ferrocenophane)^\textsuperscript{35} were unsuccessful, resulting in a number of unidentified silicon-containing products. In an attempt to attenuate the electrophilicity of a potential cationic silicon-based species, a tetramethylpiperidyl (TMP) substituted sila[1]ferrocenophane was targeted. The nitrogen atom, directly bonded to the bridging silicon atom, has the potential to stabilise a silylium ion via π-donation into the empty silicon p orbital. Hydride abstraction from this TMP-substituted sila[1]ferrocenophane will be discussed, in addition to the reactivity of sila[1]ferrocenophanes with chloro(phosphine)gold(0) complexes.

Synthesis of (2,2,6,6-tetramethylpiperidyl)sila[1]ferrocenophane (12)

In a similar manner to the synthesis of bulky sila[1]ferrocenophane 11 (Figure 4),\textsuperscript{66} which involved substitution of chlorine at silicon using Li[N(SiMe\textsubscript{3})\textsubscript{3}], the addition of 2,2,6,6-tetramethylpiperidyl lithium to a THF/hexanes solution of 10 at room temperature did not result in ring-opening of the strained monomer. Instead, nucleophilic substitution at the silicon bridging atom was found to have occurred, yielding the 2,2,6,6-tetramethylpiperidyl)sila[1]ferrocenophane 12 in 83% yield (Scheme 3).

The Si–H hydride of 12 was located at 5.6 ppm by \textsuperscript{1}H NMR spectroscopy, further upfield to that of the precursor 10 (5.9 ppm), in addition to four resonances typical of α and β-Cp protons (Figure S1). Resonances corresponding to the tetramethylpiperidyl group are observed further upfield between 1.38 and 1.61 ppm. Five resonances in the \textsuperscript{13}C NMR spectrum typical of α, β and ipso-Cp carbons were identified, along with a further four resonances corresponding to the tetramethylpiperidyl substituent (Figure S2). The \textsuperscript{29}Si(\textsuperscript{1}H) NMR spectrum (Figure S3) showed one resonance at ~32.5 ppm assigned to the bridging silicon atom, in a similar region to that of 10 (~15.4 ppm).

Abstraction of Hydride from the bridging Si centre of 12

In a series of hydride abstraction experiments, sila[1]ferrocenophane 12 was combined with an equimolar amount of trityl tetrakis(pentafluorophenyl)borate [CPh\textsubscript{3}][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] or the trityl salt of the weakly coordinating perchloro-closo-dodecarborate anion, [CPh\textsubscript{3}][B\textsubscript{12}Cl\textsubscript{12}] in a variety of aromatic solvents (chlorobenzene, 1,2-difluorobenzene, toluene, pyridine). No crystalline product could be isolated in any of these cases, but in experiments where acetonitrile was added in an attempt to stabilise the targeted silylium ion via solvent coordination (either in 1:1 stoichiometric ratio to the trityl cation, or in excess), the crystalline hexakis(acetonitrile)iron(II) salts [Fe(NCMe\textsubscript{3})\textsubscript{5}][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] and [Fe(NCMe\textsubscript{3})\textsubscript{5}][B\textsubscript{12}Cl\textsubscript{12}] were isolated (crystallographic details are provided in the Supporting Information), and no other silicon-containing products could be characterised. Salts of hexakis(acetonitrile)iron(II) paired with a variety of other anions are reported in the literature.\textsuperscript{67–71}

There are several reported examples of silyl cations stabilised via delocalisation across intra- and intermolecular 3-centre-2-electron [Si⋯H⋯Si]\textsuperscript{+} bridges.\textsuperscript{72–76} Applying this methodology to the current system, two molar equivalents of 12 to the
hydride-abstracting trityl reagent were used, but instead of the anticipated \([\text{Si} \cdots \text{H} \cdots \text{Si}]^+\) bridged product, crystalline [13][B(C6F5)4] was isolated in 7% yield (Scheme 4).²⁷

Scheme 4 Hydride abstraction from 12 and electrophilic aromatic substitution at a Cp ring by the transient silyl cation intermediate to yield [13][B(C6F5)4].

This unexpected product was isolated via slow diffusion of hexanes into the reaction solution in 1,2-difluorobenzene, and crystallises in the monoclinic space group \(P2_1\/n\) (the molecular structure of the [13]+ cation is shown in Figure 6, and \(^1\)H, \(^{13}\)C and \(^{29}\)Si NMR spectra are shown in Figures S5–7).

Fig. 6 Molecular structure of the [13]+ cation. Thermal ellipsoids displayed at the 50% probability level. Hydrogen atoms are pictured as spheres of arbitrary radii. Selected distances (Å) and angles (°): Fe(1)–Cp\textsuperscript{cent} = 1.642(2)/1.636(2), Si(1)–N(1) = 1.925(4), Fe(1)–Si(1) = 2.6547(15), \(\alpha[\text{Fe}(1)] = 20.6(2)\), \(\beta[\text{Fe}(1)] = 39.4(3)/38.9(3)\), \(\delta[\text{Fe}(1)] = 165.77(5)\), \(\theta[\text{Fe}(1)] = 97.2(2)\), Fe(2)–Cp\textsuperscript{cent} = 1.649(2)/1.638(2), Si(2)–N(2) = 1.711(4), Fe(2)–Si(2) = 2.7893(16), \(\alpha[\text{Fe}(2)] = 23.8(2)\), \(\beta[\text{Fe}(2)] = 34.9(4)/35.1(4)\), \(\delta[\text{Fe}(2)] = 161.14(5)\), \(\theta[\text{Fe}(2)] = 91.9(2)\).

Two intact sila[1]ferrocenophane units are linked via the bridging silicon of one and a \(\beta\)-Cp carbon of the other (Si(1)–C(20)). The charge of [13]+ is formally localised not at a silicon atom, but at N(1), which has been protonated to yield the
tertiary ammonium ion. The Si(1)–N(1) bond length (1.925(4) Å) is lengthened relative to both Si(2)–N(2) in [13]$^+$ (1.711(4) Å) and the Si(1)–N(1) bond in precursor 11 (1.7280(16) Å). The sum of bond angles involving the three non-protic substituents at N(1) (namely C(15)–N(1)–Si(1), C(11)–N(1)–Si(1) and C(11)–N(1)–C(15)) is 350.6°, intermediate between that expected for trigonal planar and tetrahedral geometry at nitrogen. In contrast, the sum of all bond angles at N(2) reflects trigonal planar geometry about nitrogen (361.5°). The structural differences within the sila[1]ferrocenophane (FCP) units FCP(1) and FCP(2) (defined as those based on Fe(1) and Fe(2) respectively) in [13]$^+$ are minor, although the increased tilt-angle for FCP(2) of 23.8(2)° relative to that in FCP(1) of 20.6(2)$^+$ is significant, and may be explained by the increased steric bulk attached to the Cp ring of FCP(2). Comparison of other structural parameters between FCP(1)/FCP(2) are detailed in Table 1.

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**Table 1** Important structural parameters of compounds 12, [13]$^+$ and 11. FCP(1) and FCP(2) refer to the independent sila[1]ferrocenophane units in [13]$^+$ based on Fe(1) and Fe(2) atoms respectively. Geometric parameters are depicted in Figure 1 (α = dihedral angle between the plane of each Cp ring, β = [180° − (Cp$_{\text{cent}}$–Cp$_{\text{ipso}}$–Si)] angle, δ = Cp$_{\text{cent}}$–Fe–Cp’$_{\text{cent}}$ angle, θ = Cp$_{\text{ipso}}$–Si–Cp’$_{\text{ipso}}$ angle).

It is probable that the formation of the new silicon-carbon bond in the product is a result of the electrophilic aromatic substitution of the Cp ring by a reactive cationic silicon intermediate. DFT calculations were performed to further investigate the validity of this type of bond activation (Figure 7), where an amino-stabilised silylium ion forms a Wheland-type intermediate, which rearranges in a four-membered ring transition state with Si–C bond formation and protonation of nitrogen (TS = +80 kJ mol$^{-1}$) to form the ammonium product (−93 kJ mol$^{-1}$).
Fig. 7 Calculated relative Gibbs free energies, \( \Delta G_{298} \), for the hydrogen transfer from carbon to nitrogen via the proposed Wheland intermediate. Calculations performed at the M06-2X/6-31G(d)(C,H,N,Si):SDD(Fe) level of theory. The substituents of the FCP(2) unit have been simplified to protons, and some protons have been omitted in the illustration of calculated structures.

It is interesting to note that throughout this bond activation process, all \( \text{Cp}_{ipso}-\text{Si} \) bonds remained intact, in contrast to the synthesis of \( \text{9} \) from a similar sila[1]ferrocenophane precursor. This observation is promising, as the pentacoordinate species \( \text{3} \) undergoes cationic ROP in the presence of a silylium salt. The increased bulk of \( \text{12} \) relative to \( \text{3} \) and the associated decrease in polymerisation enthalpy may account for the stability of the silyl cation intermediate with respect to ROP.

In an attempt to isolate the monomeric silyl cation, the reaction of \( \text{12} \) with one molar equivalent of trityl tetrakis(pentafluorophenyl)borate was performed at low temperature (1,2-difluorobenzene, –78 °C), but crystalline products were not isolated. It may be possible to trap the reactive silyl cation-bridged [1]ferrocenophane with a solvent molecule or Lewis base before it reacts further, much like the pyridine-stabilised silylium ion \( \text{9} \). Further attempts to isolate cations of this nature will be pursued in future work.

Reactivity of Sila[1]ferrocenophane 1 with Chloro(phosphine)gold(I)
As discussed earlier, treatment of \( \text{1} \) with HCl yields the ring-opened species \( \text{7} \) (Scheme 1). A similar reaction is observed in the case of species with B–Cl and Al–Cl bonds. However, ring-opening reactions with transition metal halides have not yet been reported. Initial investigations into the reactivity of sila[1]ferrocenophanes with chloro(trialkyl/arylphosphine)gold complexes involved attempts to functionalise monomers which featured alkyne substituents at silicon, with the aim of eventually synthesising poly(ferrocenylsilane)s with pendant gold groups (bimetallic polymers). However, the targeted ethynyl-gold complexes could not be isolated under basic conditions. Repetition of these types of experiments with the simple dimethylsila[1]ferrocenophane monomer \( \text{1} \) in the absence of base revealed a different type of reactivity (Scheme 5).

Scheme 5 Addition of Au–Cl across the \( \text{Cp}_{ipso}-\text{Si} \) bond in \( \text{1} \) to form \( \text{14} \).

Addition of AuCl(PMe\(_3\)) to \( \text{1} \) in \( \text{d}_2\)-dichloromethane yielded the ring-opened product \( \text{[1'-}(\text{chlorodimethylsilyl})-\text{ferrocenyl}][\text{trimethylphosphine})\text{gold} (\text{14}) \), which exhibited four \( \text{Cp} \) multiplets, one PMe\(_3\) doublet and one SiMe\(_2\) singlet in the \( \text{1H} \) NMR spectrum (Figure S8). \( \text{13C} \), \( \text{29Si} \) and \( \text{31P} \) NMR spectra were also consistent with this ring-opening chemistry (Figures S9, S10 and S11 respectively). Product \( \text{14} \) (which crystallises in the triclinic space group \( P \bar{1} \)) exhibits linear geometry about the gold(I) atom (Figure 8). Although spectroscopic data was consistent with formation of \( \text{14} \), satisfactory elemental analysis could not be obtained. This may be due to the presence of a small amount of CIAuPMe\(_3\), which is observed at –9.7 ppm in the \( \text{31P} \) NMR spectrum of the crystalline product (Figure S11).
Fig. 8 Molecular structure of [1′-(chlorodimethylsilyl)ferrocenyl](trimethylphosphine)gold (14). Thermal ellipsoids displayed at 50% probability level. Hydrogen atoms are pictured as spheres of arbitrary radii. Selected bond lengths (Å) and angles (°): Fe(1)–C(pent) = 1.6599(14), C(1)–Au(1) = 2.036(2), Au(1)–P(1) = 2.2812(13), Fe(1)–C(pent) = 1.6502(14), C(6)–Si(1) = 1.833(2), Si(1)–C(1) = 2.1007(13), C₉₋₆g–C₉₋₆o = Cp’cent–C₉₋₆g = 71.56(15).

Fig. 9 Reported (phosphine)gold-substituted ferrocenes.

Considering the observation that the (phosphine)gold(I) fragment is α-isolobal with a proton,97 the reaction shown in Scheme 5 is remarkably similar to the ring-opening protonolysis of sila[1]ferrocenophanes by HCl (Scheme 1). The ring-opening reaction of dimethylsila[1]ferrocenophane 1 by ClAuPPh₃ demonstrates a novel route to gold-substituted ferrocenes, in which further functionalisation may be performed by exploiting the nucleophilicity of the chlorosilane substituent.

Conclusions

The abstraction of hydride from [Fe(η-C₅H₅)Si(H)TMP] (12) was explored and an interesting product [Fe(η-C₅H₅)Si(TMP•H)(η-C₅H₅)Fe(η-C₅H₅)Si(H)TMP][B(C₆F₅)₄] containing two ferrocenophane rings was synthesised via reaction of 12 with [CPh₃][B(C₆F₅)₄]. This unusual species is proposed to have formed via electrophilic aromatic substitution of a Cp ring by a silyl cation intermediate, with subsequent protonation of the tetramethylpiperidyl substituent. The reactivity of dimethylsila[1]ferrocenophane (1) towards AuCl(PMe₃)₃ was also explored. This yielded [1′-(chlorodimethylsilyle)-ferrocenyl](trimethylphosphine)gold [Fe(C₅H₅)Si(Me₂C)(CH₂Au(PMe₃))₃] (14), and presents a novel route to gold-substituted ferrocene compounds.

Experimental

Materials and Equipment

All reactions and product manipulations of molecular species were carried out under an inert atmosphere of dinitrogen or argon using standard Schlenk line or glovebox techniques (MBraun glovebox MB150G-B maintained at < 0.1 ppm H₂O and < 0.1 ppm O₂). Dimethylsila[1]ferrocenophane (1), Chlorosila[1]ferrocenophane (10),65 and 2,2,6,6-tetramethylpiperidyllithium98 were prepared according to literature procedures. [CPh₃][B(C₆F₅)₄] was purchased from Abcr and used as received. Celite 521 was obtained from Sigma Aldrich and heated to 200 °C for 16 h prior to use. Dry...
1,2-difluorobenzene was purchased from Sigma Aldrich and stored over molecular sieves. Pyridine was purchased from Fluka and distilled from CaH₂ prior to use. Dry acetonitrile, hexanes and toluene were obtained from a Grubbs-type solvent system employing alumina and supported copper columns. THF was distilled under di-nitrogen from Na/benzophenone.

**δ (ppm) NMR spectra were recorded at ambient temperature on a Varian 500 MHz NMR spectrometer, a Jeol ECS 400 MHz NMR spectrometer and a Jeol Eclipse 300 MHz NMR spectrometer. All spectra are reported relative to external TMS and, in the cases of 1H and 13C, are referenced to the most downfield residual solvent resonance (CDCl₃: δ 7.16 ppm, δc 128.06 ppm; CD₂Cl₂: δs 5.32 ppm, δc 53.84 ppm).**

Electron ionisation (EI) mass spectra were obtained using a VG Analytical Auto-Spec mass spectrometer with a 70 eV electron impact ionisation source.

Elemental analyses were carried out by the Laboratory for Microanalysis at the University of Bristol (Model 3000 Euro EA Elemental Analyzer) using V₂O₅ to promote combustion.

Single crystal X-ray diffraction experiments for compounds 12, [13][B(C₆F₅)₄], 14, [Fe(NCMe)₃][B(C₆F₅)₄] and [Fe(NCMe)₃][B(C₂Cl₄)₂] were carried out at 100 K on a Bruker APEX II diffractometer using Mo Ka radiation (λ = 0.71073 Å). Data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre. Intensities were integrated, from several series of exposures measuring 0.5° in ω or φ. Absorption corrections were based on equivalent reflections using SADABS (compounds [13][B(C₆F₅)₄], 14, [Fe(NCMe)₃][B(C₆F₅)₄] and [Fe(NCMe)₃][B(C₂Cl₄)₂]) or TWINABS (compound 12). Structures were solved using SHELXS and refined using all F² data with hydrogen atoms located geometrically and refined using a riding model in SHELXL. Compound 12 was twinned and refined against an hk½ file. Crystallographic details provided in Tables S1–2.

DFT calculations were carried out using the Gaussian 09 Rev. 2b package of programs, using the M06-2X functional. The standard Stuttgart/Dresden ECP and associated basis set were used on iron, and the 6-31G(d) basis set on carbon, hydrogen, nitrogen and silicon.

Hydride Abstraction Reactions

Isolation of [Fe(NCMe)₃][B(C₆F₅)₄]

(2,2,6,6-Tetramethylpiperidyl)sila[1]ferrocenophane (12) (100 mg, 0.28 mmol) and [CPh₃][B(C₂Cl₄)₂] (261 mg, 0.28 mmol) were combined and dissolved in a mixture of acetonitrile (0.3 mL, 5.8 mmol, ca. 20 equiv.) and 1,2-difluorobenzene (3 mL). After stirring at room temperature for 24 h, the orange reaction solution was filtered and layered with hexanes (20 mL). Colourless crystals suitable for single crystal X-ray diffraction were grown by slow diffusion of hexanes into the 1,2-difluorobenzene/acetonitrile solution. Suitable crystals were obtained by slow diffusion of hexanes into the 1,2-difluorobenzene/acetonitrile solution. Suitable crystals were obtained by slow diffusion of hexanes into the 1,2-difluorobenzene/acetonitrile solution.

Isolation of [Fe(NCMe)₃][B(C₂Cl₄)₂]

(2,2,6,6-Tetramethylpiperidyl)sila[1]ferrocenophane (12) (100 mg, 0.28 mmol) and [CPh₃][B(C₂Cl₄)₂] (147 mg, 0.14 mmol) were combined and dissolved in acetonitrile (5 mL). Precipitation of colourless material from the red solution was observed after 1 h. The red solution was filtered and layered with toluene (20 mL), but no crystalline product was isolated. The colourless precipitate was dissolved in 1,2-difluorobenzene and layered with hexanes, and colourless crystals suitable for single crystal X-ray were isolated from this slow diffusion. Crystalllographic data is provided in the Supporting Information.

Synthesis of [13][B(C₆F₅)₄]

(2,2,6,6-Tetramethylpiperidyl)sila[1]ferrocenophane (12) (153 mg, 0.43 mmol) and [CPh₃][B(C₂Cl₄)₂] (200 mg, 0.22 mmol) were combined and dissolved in 1,2-difluorobenzene (5 mL). A colour change from red to brown/red was immediately observed. After stirring at room temperature for 1 h, the resulting solution was filtered and layered with hexanes (20 mL). Crystals of [13][B(C₆F₅)₄] suitable for single crystal X-ray diffraction were grown by slow diffusion of hexanes into a 1,2-difluorobenzene solution of the product (40 mg, 7% crystalline yield). **1H NMR (500 MHz, CDCl₃): δ (ppm) 5.59 (s, 1H, satellites: JSH = 117 Hz, Si–H), 4.99 (m, 1H, C₆H₄), 4.69 (m, 4H, C₆H₄Cl₂), 4.58 (m, 1H, C₆H₄Cl₂), 4.56 (m, 1H, C₆H₄Cl₂), 4.45 (m, 1H, C₆H₄Cl₂), 4.37 (m, 1H, C₆H₄Cl₂), 4.32–4.28 (2H, C₆H₄Cl₂), 2.22 (m, 1H, C₆H₄Cl₂), 2.19 (m, 1H, C₆H₄Cl₂), 3.94–3.90 (2H, C₂H₆, TMP), 2.05–1.94 (m, 6H, TMP),**
Synthesis of Chloro(trimethylphosphine)gold(I)

Chloro(trimethylphosphine)gold(I) was synthesised according to an adapted literature procedure.\textsuperscript{10,11} Trimethylphosphine (203 mg, 2.67 mmol) was dissolved in degassed acetone (5 mL) and added to HAuCl₃·3H₂O (500 mg, 1.27 mmol) in degassed acetone (3 mL) at 0 °C. The reaction mixture was stirred for 30 minutes, during which time the precipitation of a colourless solid was observed. The precipitate was isolated by filtration and dried to yield the product (218 mg, 0.71 mmol) in 56% yield.

Synthesis of [1\(^1\)-(chlorodimethylsilyl)-ferrocenyl](trimethylphosphine)gold(I) [14]

Dimethylsilyl[1]ferrocenophane (1) (39 mg, 0.16 mmol) and chloro(trimethylphosphine)gold (50 mg, 0.16 mmol) were combined, dissolved in CDCl₃ (5 mL) and stirred at room temperature for 16 h, over which time a colour change from red/orange to orange/yellow was observed. Crystals suitable for single crystal X-ray diffraction were grown from a CDCl₃ solution at ~40 °C to yield 54 mg of 14 as orange crystals (61% yield). \(^1\)H NMR (300 MHz, CDCl₃): \(\delta \) (ppm) 4.44 (m, 2H, H₂C₃H₃), 4.27 (m, 2H, C₃H₃₂), 4.22 (m, 2H, C₃H₃₂), 3.54 (m, 2H, C₃H₃₂), 1.51 (d, 9H, J₉H = 9.2 Hz, PMe₃), 0.76 (s, 6H, SiMe₆). \(^{13}\)C NMR (400 MHz, CDCl₃): \(\delta \) (ppm) 101.4 (d, J₉C = 130 Hz, CPₙ₉-Au), 77.4 (d, J₉C = 5.5 Hz, β-Cp), 72.0 (s, Cp), 71.3 (s, Cp), 69.9 (d, J₉C = 6.5 Hz, α-Cp), 66.6 (s, Cpₙ₉-Si), 16.0 (d, J₉C = 32.0 Hz, PMe₃), 3.13 (s, SiMe₆). \(^{31}\)Si(\(^{1}\)H) NMR (500 MHz, CDCl₃): \(\delta \) (ppm) 21.8. \(^{31}\)P(\(^{1}\)H) NMR (300 MHz, CDCl₃): \(\delta \) (ppm) 9.07. Anal. Calcd for C₁₂H₂₂AuClFePSi: C 32.72%, H 4.21%. Found: C 32.07%, H 4.02%.

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The low yield of [13][B(C6F5)4][+] suggests that it is likely not the
only product of this reaction (and therefore not a viable
synthetic route to these types of compounds), but no other
products could be identified or structurally characterised.
These two calculated structures feature an Fe atom bonded in a
dihapto fashion to the cyclopentadienyl unit. Although a
tetrahapto vs. dihapto minimum structure was not identified on the
potential energy surface, its existence cannot be ruled out.
Although protons have been shown to attack sila[1]ferrocenophanes at the Cp
ipso carbon atom, product [13]+ shows that the electrophilic attack by the siyl cation
has occurred at the β-Cp carbon atom, presumably as a result of the high steric demand of the
TMP substituent. No other transition states (for attack at the Cpipso or the α-Cp carbon atom)
could be located on the potential energy surface, but we cannot rule out the possibility that product [13]+ is one of multiple products of the reaction.
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