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

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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 -C₅H₄)Si(H)TMP] (**12**) (TMP = 2,2,6,6-tetramethylpiperidyl) towards the hydride-abstraction reagent trityl tetrakis(pentafluorophenyl)borate ([CPh₃][B(C₆F₅)₄]) was explored. This yielded the unusual dinuclear species [Fe(η -C₅H₄)₂Si(TMP•H)(η -C₅H₃Fe(η -C₅H₄)Si(H)TMP)[B(C₆F₅)₄] [**13**][B(C₆F₅)₄] 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 -C₅H₄)SiMe₂] (**1**) with the Au(I) species AuCl(PMe₃). This was found to result in addition of the Au–Cl bond across the Cp_{ipso}–Si bond, to yield the ring-opened species [1'-(chlorodimethylsilyl)-ferrocenyl](trimethylphosphine)gold(I), [Fe(C₅H₄Si(Me₂Cl)(C₅H₄Au(PMe₃))] (**14**). This represents the first example of ring-opening addition of a metallocenophane with a reagent possessing a transition metal-halogen bond.

Introduction

Within a decade of the discovery of ferrocene in the 1950s, the first *ansa*-metallocenes, or [*n*]metallocenophanes, were prepared.^{1,2} [*n*]Metallocenophanes (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*]metallocenophanes, 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 d⁶–d⁸ metals), ring-tilted structure.

[*n*]Ferrocenophanes bridged by a single silicon atom were among the first [*n*]metallocenophanes to be reported,¹⁴ and they are at present widely employed as precursors to poly(ferrocenylsilane)s 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 stannynes.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 Cp_{ipso}–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 sp² Cp_{ipso} 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° – (Cp_{cent}–Cp_{ipso}–Si)] angle, δ = Cp_{cent}–Fe–Cp_{cent} angle, θ = Cp_{ipso}–Si–Cp'ipso angle.

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 pendent group in these molecules

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results in lengthening of the *trans* Cp_{ipso}–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 (R₃Si⁺) are considered to have been isolated, where no stabilisation by counter-anions or solvent molecules is evident; namely (Mes)₃Si⁺,^{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 silylium ions the charge is predominantly localised at the silicon atom due to the lower tendency for hyperconjugation with the diffuse valence orbitals of silicon,⁴⁹ resulting in reaction with many weak σ- and π-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 α-ferrocenyl silyl cation in compound **6** and the isoelectronic borane and carbenium analogues (Figure 3).^{59, 60}

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

In all cases, a “dip angle”, α^* (defined as $[180^\circ - (\text{Cp}_{\text{cent}} - \text{Cp}_{\text{ipso}} - \text{E})]$ angle) of the electron-deficient α-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 (Cp_{ipso}–Si–Fe of the upper ring, and Fe–Si–C of

the lower ring), accounting for the particularly large dip angle.⁶¹ In this respect, bonding of both Cp rings to Si is reminiscent of *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.^{62, 63} Ring-opening protonolysis of sila[1]ferrocenophanes with HCl has been shown to yield ferrocenylchlorosilanes (Scheme 1),⁴⁰ but the analogous reaction of di(ferrocenyl)sila[1]ferrocenophane (**8**)⁶⁴ and HBF₄ yielded a mixture of ferrocenylfluorosilanes, thought to proceed via extraction of F[−] from [BF₄][−] by a reactive silicon-based intermediate. Employing ‘Brookhart’s acid’ with weakly coordinating [3,5-bis(trifluoromethyl)phenyl]borate anion (Scheme 2),⁶⁵ the pyridine-coordinated silyl cation **9** was isolated, exhibiting geometry at silicon intermediate between trigonal planar and tetrahedral.⁶² 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.

Scheme 2 Ring-opening protonation of di(ferrocenyl)sila[1]ferrocenophane **8** to yield silyl cation **9**.

The syntheses of ferrocene-substituted silylium ions **6**^{56–58, 61} and **9**⁶² rely on very different methodologies. The first involves hydride abstraction from silicon using the trityl cation ([CPh₃]⁺), 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 Cp_{ipso}–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)³³ were unsuccessful, resulting in a number of unidentifiable 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(I) 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),⁶⁶ which involved substitution of chlorine at silicon using $\text{LiN}(\text{SiMe}_3)_2$, the addition of 2,2,6,6-tetramethylpiperidyllithium 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).

Fig. 4 Sila[1]ferrocenophanes bearing chloro- and bis(trimethylsilyl)amino- substituents.

The Si–H hydride of **12** was located at 5.6 ppm by ^1H 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 ^{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 $^{29}\text{Si}\{^1\text{H}\}$ 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).

Scheme 3 Synthesis of (2,2,6,6-tetramethylpiperidyl)sila[1]ferrocenophane (**12**).

The orange/red product **12** was isolated from hexanes at -40 °C and found to crystallise in the orthorhombic space group *Iba*2. The molecular structure of **12**, shown in Figure 5, exhibits structural parameters similar to those of the related sila[1]ferrocenophane **11**, which also features a bulky amino-based group at the bridging silicon (Table 1).

Fig. 5 Molecular structure of (2,2,6,6-tetramethylpiperidyl)sila[1]ferrocenophane (**12**). Thermal ellipsoids displayed at the 50% probability level. Hydrogen atoms are pictured as spheres of arbitrary radii. Selected distances (Å) and angles (°):

$\text{Fe}(1)\text{--Cp}_{\text{cent}} = 1.6371(7)/1.6353(8)$, $\text{Si}(1)\text{--N}(1) = 1.7280(16)$, $\text{Fe}(1)\cdots\text{Si}(1) = 2.7350(6)$, $\alpha = 21.89(8)$, $\beta = 36.21(14)/36.74(14)$, $\delta = 163.675(16)$, $\theta = 93.73(9)$.

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 $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ or the trityl salt of the weakly coordinating perchloro-closo-dodecaborate anion, $[\text{CPh}_3][\text{B}_{12}\text{Cl}_{12}]$ 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 $[\text{Fe}(\text{NCMe})_6][\text{B}(\text{C}_6\text{F}_5)_4]_2$ and $[\text{Fe}(\text{NCMe})_6][\text{B}_{12}\text{Cl}_{12}]$ 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.^{67–71}

There are several reported examples of silyl cations stabilised via delocalisation across intra- and intermolecular 3-centre-2-electron $[\text{Si}\cdots\text{H}\cdots\text{Si}]^+$ bridges.^{72–76} Applying this methodology to the current system, two molar equivalents of **12** to the

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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).⁷⁷

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 ¹H, ¹³C and ²⁹Si 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_{cent} = 1.642(2)/1.636(2), Si(1)–N(1) = 1.925(4), Fe(1)⋯Si(1) = 2.6547(15), α[Fe(1)] = 20.6(2), β[Fe(1)] = 39.4(3)/38.9(3), δ[Fe(1)] = 165.77(5), θ[Fe(1)] = 97.2(2), Fe(2)–Cp_{cent} = 1.649(2)/1.638(2), Si(2)–N(2) = 1.711(4), Fe(2)⋯Si(2) = 2.7893(16), α[Fe(2)] = 23.8(2), β[Fe(2)] = 34.9(4)/35.1(4), δ[Fe(2)] = 161.14(5), θ[Fe(2)] = 91.9(2).

Two intact sila[1]ferrocenophane units are linked via the bridging silicon of one and a β-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.

	12	[13]⁺		11
		FCP(1)	FCP(2)	
α , °	21.89(8)	20.6(2)	23.8(2)	21.01(15)
β , °	36.21(14)	39.4(3)	34.9(4)	37.1(3)
	36.74(14)	38.9(3)	35.1(4)	37.5(3)
δ , °	163.675(16)	165.77(5)	161.14(5)	164.71(10)
θ , °	93.73(9)	97.2(2)	91.9(2)	95.14(16)
Fe–Cp _{cent} , Å	1.6371(7)	1.642(2)	1.649(2)	1.6381(17)
	1.6353(8)	1.636(2)	1.638(2)	1.6414(16)
Fe...Si, Å	2.7350(6)	2.6547(15)	2.7893(16)	2.7025(12)
Si–N, Å	1.7280(16)	1.925(4)	1.711(4)	1.719(4)

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 = $[180^\circ - (\text{Cp}_{\text{cent}} - \text{Cp}_{\text{ipso}} - \text{Si})]$ angle, δ = $\text{Cp}_{\text{cent}} - \text{Fe} - \text{Cp}'_{\text{cent}}$ angle, θ = $\text{Cp}_{\text{ipso}} - \text{Si} - \text{Cp}'_{\text{ipso}}$ 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,⁷⁸ 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}).⁷⁹

Fig. 7 Calculated relative Gibbs free energies, G^{298} , for the hydrogen transfer from carbon to nitrogen via the proposed Wheland intermediate. Calculations performed at the M06-2X⁸⁰/6-31G(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 $\text{Cp}_{\text{ipso}}\text{-Si}$ bonds remained intact, in contrast to the synthesis of **9** from a similar sila[1]ferrocenophane precursor. This observation is promising, as the pentacoordinate species **3** undergoes cationic ROP in the presence of a silylium salt. The increased bulk of **12** relative to **3** and the associated decrease in polymerisation enthalpy may account for the stability of the silyl cation intermediate with respect to ROP.⁶⁶ In an attempt to isolate the monomeric silyl cation, the reaction of **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 **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 **1** with HCl yields the ring-opened species **7** (Scheme 1). A similar reaction is observed in the case of species with B-Cl and Al-Cl bonds.^{81, 82} 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^{83, 84} involved attempts to functionalise monomers which featured alkyne substituents at silicon,⁸⁵ 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 **1** in the absence of base revealed a different type of reactivity (Scheme 5).

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

Addition of $\text{AuCl}(\text{PMe}_3)$ to **1** in d_2 -dichloromethane yielded the ring-opened product [1'-(chlorodimethylsilyl)-ferrocenyl](trimethylphosphine)gold (**14**), which exhibited four Cp multiplets, one PMe_3 doublet and one SiMe_2 singlet in the ^1H NMR spectrum (Figure S8). ^{13}C , ^{29}Si and ^{31}P NMR spectra were also consistent with this ring-opening chemistry (Figures S9, S10 and S11 respectively). Product **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 **14**, satisfactory elemental analysis could not be obtained. This may be due to the presence of a small amount of ClAuPMe_3 , which is observed at -9.7 ppm in the ^{31}P 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)–Cpcent = 1.6599(14), C(1)–Au(1) = 2.036(2), Au(1)–P(1) = 2.2812(13), Fe(1)–Cp'cent = 1.6502(14), C(6)–Si(1) = 1.833(2), Si(1)–C(1) = 2.1007(13), Cp_{ipso}–Cp_{cent}–Cp'cent–Cp'ipso = 71.56(15).

Relatively few metallocenyl-gold complexes have been reported,^{86–92} and they are of interest as a result of gold(I) catalysis in general, in addition to the catalytic efficiency which is observed for metallocene-based metallacycles.^{93, 94} Metallation of ferrocene can be achieved with lithium, magnesium, mercury and tin. The auration of ferrocene was first reported in 1969 and involved reaction of lithioferrocene with ClAuPPh₃.⁹⁵ Synthetic routes to ferrocenyl-(phosphine)gold complexes involve reactions of lithiated ferrocene derivatives and ClAuPR₃ reagents.^{87, 88} In most of these cases (compounds **15**–**20**), the substituted ferrocene with an R' group directs the lithiation to an adjacent site on same Cp ring, and therefore the disubstituted ferrocenyl-(phosphine)gold complexes that have been reported to date do not include any in which both Cp rings of the ferrocene unit are functionalised (Figure 9). Recently, an alternative synthesis was also reported, involving the transmetalation of various (phosphine)gold(I) bromide compounds with arylboronic acids in the presence of base to yield the monosubstituted ferrocene compound **16** and diphosphine derivative **24**.^{86, 96} The unusual dinuclear chiral complex **25** was synthesised from Me₂SAuCl and a lithiated ferrocene precursor, and features an intramolecular Au(I)···Au(I) distance of 2.85 Å.⁹⁰

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

Considering the observation that the (phosphine)gold(I) fragment is σ -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 ClAuPR₃ 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 -C₅H₄)Si(H)TMP] (**12**) was explored and an interesting product [Fe(η -C₅H₄)₂Si(TMP•H)(η -C₅H₃)Fe(η -C₅H₄)Si(H)TMP][B(C₆F₅)₄] [**13**][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) was also explored. This yielded [1'-(chlorodimethylsilyl)-ferrocenyl](trimethylphosphine)gold [Fe(C₅H₄Si(Me₂Cl)(C₅H₄Au(PMe₃))] (**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**),³⁹ Chlorosila[1]ferrocenophane (**10**),⁶⁶ 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

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1,2-difluorobenzene was purchased from Sigma Aldrich and stored over molecular sieves. Pyridine was purchased from Fluka and distilled from CaH_2 prior to use. Dry acetonitrile, hexanes and toluene were obtained from a Grubbs-type solvent system employing alumina and supported copper columns.⁹⁹ THF was distilled under dinitrogen from Na/benzophenone.

^1H , ^{13}C , ^{29}Si and ^{31}P 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 ^{13}C , are referenced to the most downfield residual solvent resonance (C_6D_6 : δ_{H} 7.16 ppm, δ_{C} 128.06 ppm; CD_2Cl_2 : δ_{H} 5.32 ppm, δ_{C} 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 V_2O_5 to promote combustion.

Single crystal X-ray diffraction experiments for compounds **12**, **[13][B(C₆F₅)₄]**, **14**, **[Fe(NCMe)₆][B(C₆F₅)₄]₂** and **[Fe(NCMe)₆][B₁₂Cl₁₂]** were carried out at 100 K on a Bruker APEX II diffractometer using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre. Intensities were integrated,¹⁰⁰ 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)₆][B(C₆F₅)₄]₂** and **[Fe(NCMe)₆][B₁₂Cl₁₂]**) or TWINABS (compound **12**).¹⁰¹ The structures were solved using SHELXS and refined against all F_o^2 data with hydrogen atoms located geometrically and refined using a riding model in SHELXL.¹⁰² Compound **12** was twinned and refined against an hklf5 file. Crystallographic details provided in Tables S1–2.

DFT calculations were carried out using the Gaussian 09 Rev. 2b package of programs,¹⁰³ using the M06-2X functional.⁸⁰ The standard Stuttgart/Dresden ECP and associated basis set were used on iron,¹⁰⁴ and the 6-31G(d) basis set on carbon, hydrogen, nitrogen and silicon.^{105, 106} The M06-2X global hybrid functional with the 6-31G(d) basis set is a well-established level of theory in the computational chemistry of organic and organometallic compounds,¹⁰⁷ and the closely related M05-2X/6-31G(d) level of theory has recently been shown to be adequate for silyl cationic compounds.¹⁰⁸ The transition state was located by using the Synchronous Transit-Guided Quasi-Newton (STQN) method, using the optimised structures of the starting complex (Wheland intermediate) and the end product. All stationary points were characterised as minima or transition states (maxima), respectively, by analytical vibrational frequency calculations. Frequency calculations were used to compute zero-point energies and to derive values for free energy, G^{298} . Atomic coordinates are provided in the Supporting Information.

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

Chlorosila[1]ferrocenophane (**10**) (500 mg, 2.01 mmol) and 2,2,6,6-tetramethylpiperidyllithium (296 mg, 2.01 mmol) were

dissolved in hexanes:THF (1:2, 10 mL) and stirred at room temperature for 24 h. The solvent was removed in vacuo from the resulting red solution. Hexanes (10 mL) was added and lithium chloride was removed by filtration. The product (**12**) was recrystallised from hexanes at -40°C to yield 590 mg of orange/red crystals (83% yield) suitable for single crystal X-ray diffraction. ^1H NMR (500 MHz, C_6D_6): δ (ppm) 5.64 (s, 1H, satellites: $J_{\text{SiH}} = 113 \text{ Hz}$, Si–H), 4.41 (t, 2H, C_5H_4), 4.30 (t, 2H, C_5H_4), 4.26 (t, 2H, C_5H_4), 4.23 (t, 2H, C_5H_4), 1.61 (s, 12H, Me), 1.54 (m, 2H, NCH_2CH_2), 1.38 (m, 4H, NCH_2CH_2). ^{13}C NMR (500 MHz, C_6D_6): δ (ppm) 77.37 (Cp), 76.23 (Cp), 75.52 (Cp), 75.34 (Cp), 53.79 ($\text{NC}(\text{CH}_3)_2$), 42.88 ($\text{NC}(\text{CH}_3)_2\text{CH}_2$), 39.94 (Cp_{ipso}), 32.86 ($\text{NC}(\text{CH}_3)_2$), 18.08 ($\text{NC}(\text{CH}_3)_2\text{CH}_2\text{CH}_2$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (500 MHz, C_6D_6): δ (ppm) -32.5 . EI-MS (positive ion mode, THF/MeCN): m/z 213.0 $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{SiH}]^+$, 338.1 $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{SiH}(\text{C}_8\text{H}_{15}\text{N})]^+$, 353.1259 $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2\text{SiH}(\text{C}_9\text{H}_{18}\text{N})]^+$ (**[12]⁺**) (Figure S4). Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{FeNSi}$: C 64.58%, H 7.70%, N 3.96%. Found: C 64.39%, H 7.53%, N 3.82%.

Hydride Abstraction Reactions

Isolation of **[Fe(NCMe)₆][B(C₆F₅)₄]₂**.

(2,2,6,6-Tetramethylpiperidyl)sila[1]ferrocenophane (**12**) (100 mg, 0.28 mmol) and $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (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. Crystallographic data is provided in the Supporting Information.

Isolation of **[Fe(NCMe)₆][B₁₂Cl₁₂]**.

(2,2,6,6-Tetramethylpiperidyl)sila[1]ferrocenophane (**12**) (100 mg, 0.28 mmol) and $[\text{CPh}_3]_2[\text{B}_{12}\text{Cl}_{12}]$ (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. Crystallographic 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 $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (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, C_6D_6): δ (ppm) 5.59 (s, 1H, satellites: $J_{\text{SiH}} = 117 \text{ Hz}$, Si–H), 4.99 (m, 1H, C_5H_4), 4.69 (m, 4H, C_5H_4), 4.58 (m, 1H, C_5H_4), 4.56 (m, 1H, C_5H_4), 4.45 (m, 1H, C_5H_4), 4.37 (m, 1H, C_5H_4), 4.32–4.28 (m, 2H, C_5H_4), 4.22 (m, 1H, C_5H_4), 4.19 (m, 1H, C_5H_4), 3.94–3.90 (m, 2H, C_5H_4), 2.05–1.94 (m, 6H, TMP),

1.78–1.74 (m, 12H, TMP), 1.69–1.47 (m, 18H, TMP). ^{13}C NMR (500 MHz, C_6D_6): δ (ppm) 83.10, 80.60, 80.28, 80.13, 79.91, 79.66, 77.75, 77.21, 76.94, 76.83, 76.09, 75.83, 75.55, 74.80, 64.95, 63.73 (Cp), 53.77 (FCP(2) TMP), 48.16, 44.77 (FCP(1) Cp_{ipso}), 42.00 (FCP(2) TMP), 40.60, 40.19 (FCP(2) Cp_{ipso}), 32.56 (FCP(2) TMP), 32.33, 32.11, 31.86, 26.99, 24.86, 23.61 (FCP(1) TMP), 17.54 (FCP(2) TMP), 15.38 (FCP(1) TMP). $^{29}\text{Si}\{^1\text{H}\}$ NMR (500 MHz, C_6D_6): δ (ppm) –33.5 (Si–H), –0.9 (Si–NH). Anal. Calcd for $\text{C}_{62}\text{H}_{53}\text{BF}_{20}\text{Fe}_2\text{N}_2\text{Si}_2$: C 53.78%, H 3.86%, N 2.02%. Found: C 53.29%, H 4.06%, N 2.00%.

Synthesis of Chloro(trimethylphosphine)gold(I)

Chloro(trimethylphosphine)gold(I) was synthesised according to an adapted literature procedure.^{109, 110} Trimethylphosphine (203 mg, 2.67 mmol) was dissolved in degassed acetone (5 mL) and added to $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (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'-(chlorodimethylsilyl)-ferrocenyl](trimethylphosphine)gold(I) (14)

Dimethylsila[1]ferrocenophane (1) (39 mg, 0.16 mmol) and chloro(trimethylphosphine)gold (50 mg, 0.16 mmol) were combined, dissolved in CDCl_3 (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 CDCl_3 solution at –40 °C to yield 54 mg of 14 as orange crystals (61% yield). ^1H NMR (300 MHz, CDCl_3): δ (ppm) 4.44 (m, 2H, C_5H_4), 4.27 (m, 2H, C_5H_4), 4.22 (m, 2H, C_5H_4), 3.94 (m, 2H, C_5H_4), 1.51 (d, 9H, $J_{\text{PH}} = 9.2$ Hz, PMe_3), 0.76 (s, 6H, SiMe_2). ^{13}C NMR (400 MHz, CDCl_3): δ (ppm) 101.4 (d, $J_{\text{PC}} = 130$ Hz, $\text{Cp}_{\text{ipso}}\text{--Au}$), 77.4 (d, $J_{\text{PC}} = 5.5$ Hz, $\beta\text{--Cp}$), 72.0 (s, Cp'), 71.3 (s, Cp'), 69.9 (d, $J_{\text{PC}} = 6.5$ Hz, $\alpha\text{--Cp}$), 66.6 (s, $\text{Cp}'_{\text{ipso}}\text{--Si}$), 16.0 (d, $J_{\text{PC}} = 32.0$ Hz, PMe_3), 3.13 (s, SiMe_2). $^{29}\text{Si}\{^1\text{H}\}$ NMR (500 MHz, CDCl_3): δ (ppm) 21.8. $^{31}\text{P}\{^1\text{H}\}$ NMR (300 MHz, CDCl_3): δ (ppm) 9.07. Anal. Calcd for $\text{C}_{15}\text{H}_{23}\text{AuClFePSi}$: C 32.72%, H 4.21%. Found: C 32.07%, H 4.02%.

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77. 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.
78. 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.
79. 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 silyl 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 Cp_{ipso} 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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