Journal of Organometallic Chemistry 694 (2009) 2020–2028

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

The highly regiospecific synthesis and crystal structure determination of 1,1′-2,5′ substituted ring-locked ferrocenes

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ARTICLE INFO

Article history:
Received 6 November 2008
Received in revised form 20 January 2009
Accepted 28 January 2009
Available online 5 February 2009

Keywords:
1,1′ 2,5′-Ferrocene derivatives
*Ortho*lithiation
Ferroceneophane
Ring-locked
Regiospecific
Chiral

ABSTRACT

1,1′-Ferrocene biscarboxaldehyde (**1**) has been prepared and the aldehyde groups were subsequently protected with acetal groups to produce 1,1′-bisacetalferrocene (**2**). A ring-locked ferrocene was synthesised by further derivatisation of the cyclopentadiene rings at the 2,2′ positions with phosphine substituents to produce 2,2′-bis-(acetal)-1,1′-diphenylphosphinoferrocene (**3**), which was subsequently coordinated to either a nickel chloride (**5**) or nickel bromide (**6**) metal centre. The ring-locked ferrocene complexes produced 2,5′-bis-(acetal)-1,1′-diphenylphosphinoferrocene substitution patterns. The acetal protecting groups of 2,2′-bis-(acetal)-1,1′-diphenylphosphinoferrocene were removed to produce 1,1′-bis-carboxaldehyde-2,2′-diphenylphosphinoferrocene (**4**). The Cp rings of 1,1′-bisacetalferrocene were also further derivatised at the 2,2′ positions with a silane to produce the ring-locked 1,1′-siloxane-2,5′-bisacetalferrocenophane (**7**). The acetal protecting groups were removed from this to produce 1,1′-siloxane-2,5′-ferrocenophanecarboxaldehyde (**8**). For both the phosphine and siloxane electrophiles, the substitution on the Cp rings gives chiral products (obtained as racemic mixtures). Due to the highly regioselective nature of the reaction and diastereoselectivity in the products only C_2-symmetric compounds were observed without the presence of meso diastereoisomers. Subsequent ring-locking forced the Cp rings to rotate, leading to 1,1′-ring-locked ferrocenes with 2,5′-arrangement of the acetal groups (i.e. on opposite faces of the ferrocene unit).

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1. Introduction

Substituted ferrocenes are useful compounds in catalysis and molecular electronics and this requires regioselective synthesis of target ferrocenes. *Ortho*lithiation is a versatile tool to achieve 1,1′,2,2′-substituted ferrocenes and ring-locked ferrocenes have been widely studied [1,2]. Here, we have investigated combining these two strategies for the regioselective derivatisation of ferrocene. This approach is important to produce key target molecules; for example, important targets for conducting polymers and molecular wires are poly-1,1′-ethynylferrocenes. To produce such targets, the synthesis of 1,1′-ethynylferrocene must first be achieved. However, previous attempts to produce this monomer have suffered intramolecular dimerisation of the ethynyl groups, generating a ferrocenophane [1]. To try to prevent this, Pudelski et al. reported the synthesis and deprotection of 1,1′-bis((trimethylsilyl)ethynyl)ferrocene precursors [1,2]. However, on deprotection, these molecules underwent rapid intramolecular coupling to form ferrocenophanes rather than the desired bis-ethynyl ferrocene. In related work, Ingham et al. reported the synthesis of monomeric, dimeric and polymeric ferrocenylacetylides such as 1,1′-bis(phenylethynyl)ferrocene [3] by coupling 1,1′-diiodoferrocene with a specific quantity of phenyltrimethylstannane derivatives using $Pd(PPh_3)_4$ as a catalyst.

Butler et al. reported key monomers for poly-1,1′-ethynylferrocene using 1′–bromo- and 1′-iodoferrocenylethyne in a selective coupling sequence [4]. This did produce the desired polymer but the synthesis was limited by the number of by-products including oligomers and ferrocene dimeric diynes. Ethynyl groups have also been used to attach ferrocene units to conducting polymers [5,6] and alkyne groups have been used to link ferrocene to chromophores (e.g. ferrocenylanthracenes and ferrocenyl bipyridines) by palladium-catalysed coupling [7]. Other examples of ferrocenyl linkages include the first bis-alkynylferrocene complexes with fluorene spacers [8] and dyads and polyads of ferrocenylanthraquinones, acridones and acridines [9–11]. Ethynyl ferrocene spacer groups have also been attached to terpyridyl units by coupling a terminal acetylene group to 4′-[[(trifluoromethyl)sulfinyl]oxy]-2,2′:6,2″-terpyridine using a $Pd(PPh_3)_4$ catalyst, with these compounds showing fast quantitative information transfer in work aimed at developing molecular wires [12,13]. In a related study,

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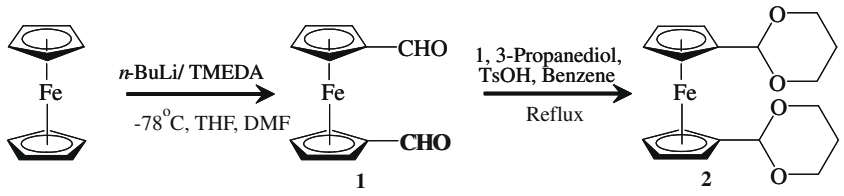
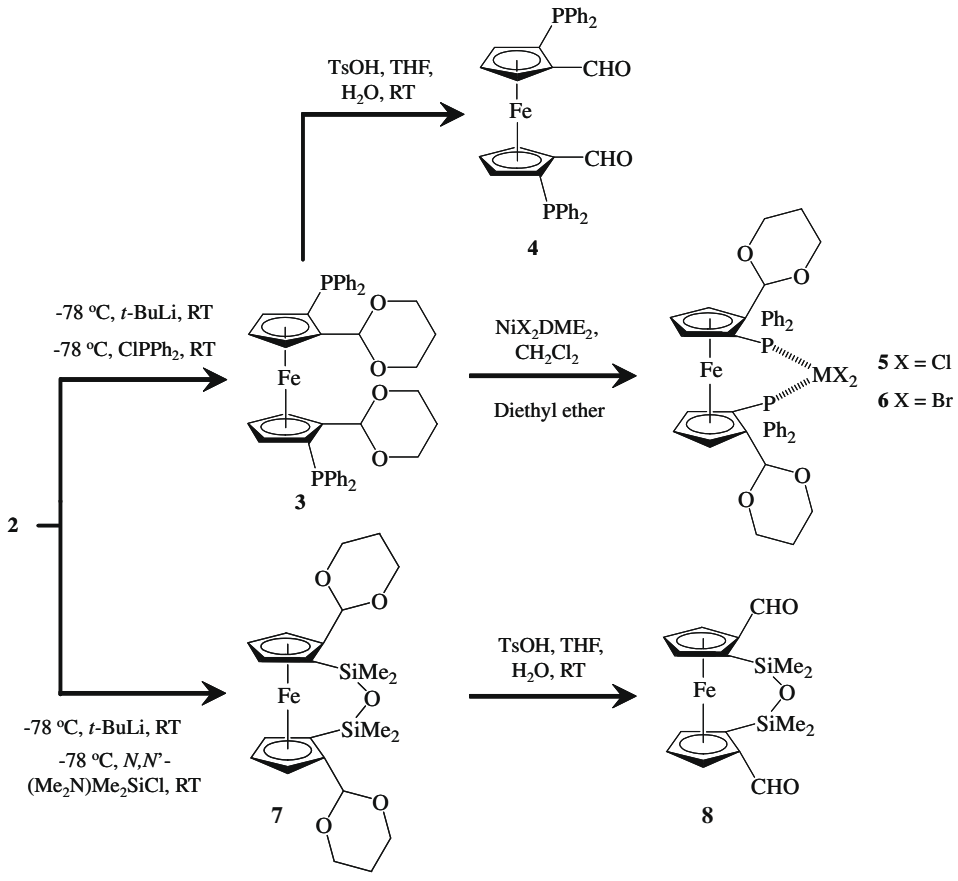
doi:10.1016/j.jorganchem.2009.01.049

Long et al. reported the synthesis of alkynylferrocene and biferrocene ligands and their platinum-containing dimers and oligomers [14] to study the electronic interaction between organometallic units and the donor/acceptor role of the platinum. Similar studies have been reported for ferrocene units bridged by silane or sulfide spacers [15].

In this paper, the synthetic strategy adopted has been to prepare 1,1′-ring-locked ferrocenes to prevent rotation of the cyclopentadienyl groups and to achieve 2,5′-substitution of the Cp rings to produce substituents on the top and bottom rings on opposite sides of the ring lock (Schemes 1 and 2). This type of approach could, in the future, be used to prevent intramolecular dimerisation of 1,1′-ethynylferrocene and hence lead to poly-1,1′-ethynylferrocene. In this study, electrophilic substitution on the Cp rings gives chiral products (obtained as racemic mixtures). Due to the highly regioselective nature of the reaction and diastereoselectivity in the products only C_2-symmetric compounds were observed without the presence of meso diastereoisomers. Most reports for synthesising tetrasubstituted ferrocenes follow a diastereoselective *ortho*lithiation strategy applied to ferrocenes bearing one chiral directing group on each Cp ring. The chiral directing groups used have included an amino group [17], an oxazoline [18], and further work by Balavoine et al. who reported variations in the diastereoselectivity after ortholithiation of the 1,1′-bis-aminoalkoxide [19,20] and 1,1′-bisacetal [16]. Ortholithiation of the latter was highly regioselective towards formation of the meso diastereoisomer with an overall yield of 8% reported [16]. By changing the protecting group to an aminoalkoxide, the regioselective nature of the reaction changes and the diastereoselective formation of C_2-symmetric tetrasubstituted ferrocenes was favoured giving an overall yield of 28% with an enantiomeric excess >99% [19,20]. In both cases, the ferrocenophane was formed by deprotecting and reducing the aldehydes to alcohols, then dehydrating to lock the Cp rings *via* an ether group. of the Such C_2-symmetric tetrasubstituted ferrocenes have already found successful application in asymmetric catalysis, e.g. palladium-catalysed asymmetric cross-coupling [17] and asymmetric allylic substitution [21]. In this paper, aldehyde groups protected using 1,3-propanediol were chosen as pre-



Scheme 1.



Scheme 2.

cursors to the acetylene function. The protection of ferrocenecarboxaldehyde with 1,3-propanediol has been reported during the preparation of ethynylferrocenes including the first 1,2,3,4,5-pentaethynyl derivative [22–24].

Ferrocene is conveniently disubstituted using a range of precursors such as 1,1′-bishalomercurioferrocene or 1,1′-ferrocenylboronic acid [25,26]; however, the dilithium salt formed *in situ* by treatment with butyllithium and tetramethylethylenediamine (TMEDA) is considered the most practical [27–29].

This paper reports the investigation of the regioselective synthesis of 1,1′-2,2′-substituted ferrocenes by *ortho*lithiation of acetal-protected precursors, followed by ring-locking to produce either a nickel halide complex with phosphine ligands or *via* a siloxane-bridged ferrocenophane to produce 1,1′-2,5′-substituted ferrocenes. Deprotection of the acetal protecting groups to form the corresponding aldehyde-bearing compounds is also described.

2. Results and discussion

The strategy used in this work was to prepare a ring-locked ferrocenophane containing precursors to 1,1′-ethynyl groups. Two ring-locked ferrocenes have been synthesised; the first using metal phosphines complexed to a metal centre (Scheme 1) and the second using a siloxane bridge (Scheme 2). The overall aim, in each case, has been to ensure the ethynyl-precursor functional groups are orientated on opposite faces of the upper and lower Cp rings of the ferrocene to prevent intramolecular coupling.

1,1′-Ferrocenecarbaldehyde **(1)** was prepared using literature methods [28] and the product identified using ^{1}H and ^{13}C NMR and elemental analysis, which were consistent with the data previously reported in the literature [28,29] Compound **(1)** was converted to 1,1′-bisacetalferrocene **(2)** with 1,3-propanediol using the conditions reported by Steffen et al. for the synthesis of monoacetalferrocene from ferrocenecarboxaldehyde [22]. To the best of our knowledge **(2)** reported in this work has only been reported once in the literature [30]. This is due to the preferred use of chiral acetal groups during the preparation of formyl scaffolds, although it has been reported that a similar acetal group (using 1,1-ethanediol) has been used for the partial protection of 1,1′-ferrocenecarbaldehyde [31].

Compound **(2)** was obtained in 81% yield and it was crystallographically analysed. The yield is higher than the 63% quoted in the literature [30]. Two broad singlets are present in the ferrocene region corresponding to the α and β hydrogens of each Cp ring [28]. Resonances for the acetal group protons were identified by comparison with the data reported by Steffen et al. for the monoacetal prepared from ferrocenecarboxaldehyde [22]. ^{13}C NMR data show three resonances in the ferrocene region and three resonances for the acetal group carbons, which is consistent with the structure. A clean molecular ion was observed in the mass spectrum. In addition, saturated C–H and C–O stretches for the acetal group are observed by infrared spectroscopy. Finally, the structure was confirmed using X-ray crystallography. The molecular structure of (**2**) is shown in Fig. 1.

Compound **(2)** was then lithiated using similar conditions previously reported in the literature by Balavoine et al. for the 1,1′ ortholithiation of the corresponding chiral 1,1′- bisacetalferrocene [16]. However, in this case, lithiation was followed by reaction with $ClPPh_2$ to give the chiral 1,1′,2,2′-tetrasubstituted product **(3)** in 62% yield (obtained as a racemic mixture) with no trisubstituted ferrocenes being isolated from the reaction. Due to the highly regioselective nature of the reaction and diastereoselectivity in the products only C_2-symmetric compounds were observed (i.e. the acetal groups are oriented as shown in Scheme 2) without the presence of the meso diastereoisomer. By comparison, Balavoine et al. reported that the major product of their reaction was the 1,2,1′-trisubstituted molecule; the desired 1,1′,2,2′-tetrasubstituted product was diastereoselective towards the meso diastereomer, which, was obtained in 8% yield [16]. Interestingly, it has been reported recently that larger, methoxy-substituted (chiral) acetal groups can cause problems during attempted ortholithiation of the Cp ring [32]. It may be that the larger acetal group bulk caused steric hindrance for the butyllithium base during attempted ortholithiation. It has also been reported that there can be competition between proton abstraction and nucleophilic attack with methoxy groups attached to the acetal group [32]. However, this was not the case for the simple non-chiral acetal group used in this work. In addition, the acetal group remains intact during reaction, meaning it should be possible to further derivatise the products to prepare 1,1′,2,2′,3,3′-substituted ferrocenes.

Compound **(3)** has not previously been reported in the primary literature. Compound **(3)** was analysed by ^{1}H and ^{13}C NMR, mass

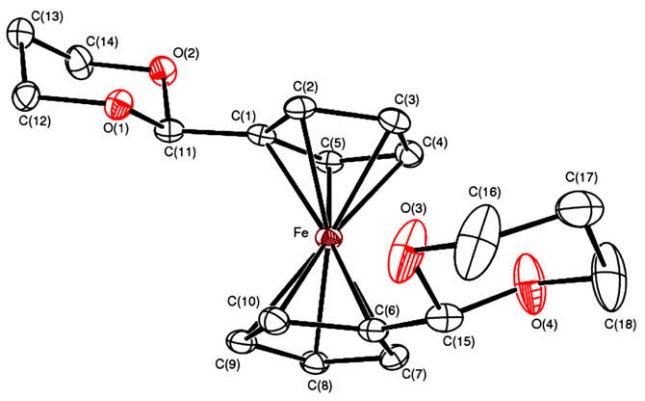


Fig. 1. Molecular structure of (**2**). In Figs. 1–7 displacement ellipsoids are drawn at the 30% probability level and all hydrogen atoms are omitted for clarity.

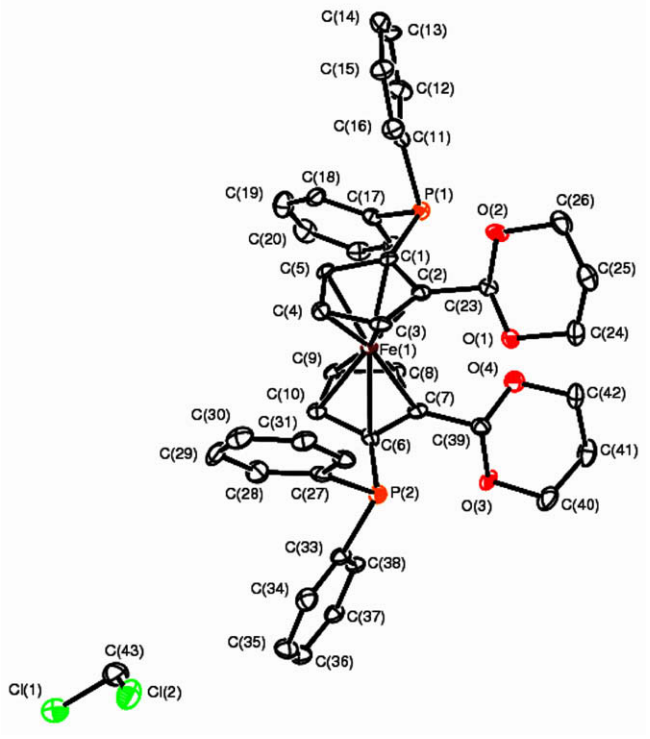


Fig. 2. Molecular structure of (**3**).

spectrometry with accurate mass measurement, IR spectroscopy, and elemental analysis. The relative orientation of the functional groups on the Cp rings is confirmed by X-ray crystallography (Fig. 2) as the desired C_2 symmetrically substituted isomer. Trace peaks in the ^{1}H NMR spectrum are ascribed to small amounts of oxidation of the phosphine ligands; this is supported by the presence of a second small peak in the ^{31}P NMR for phosphine oxide. Deprotection of **(3)** gives the phosphine aldehyde **(4)** with C_2 symmetry (Fig. 3) but attempts to synthesise a ring-locked complex from **(4)** by coordination to nickel(II) bromide proved unsuccessful. However, coordination of **(3)** to nickel(II) chloride gave **(5)** and with nickel(II) bromide gave **(6)**; both gave crystal structures with the orientation expected for the C_2 symmetrically substituted isomer (Figs. 4 and 5, respectively). A clean molecular ion of (**6**) was observed in the mass spectrum whilst mass spectrometry of (**5**) showed only a clean molecular ion of (m/z = 726.1749) which corresponds to the uncomplexed diphosphinoferrocene (**3**) in EI and FAB modes implying a weakly-bound complex for (**5**). Characterisation of compounds **(5)** and **(6)** was attempted using NMR and elemental analysis. A very broad set of resonances was shown on the ^{1}H NMR spectrum, which, could not be assigned to the ferrocene or acetal hydrogens. In addition, ^{13}C and ^{31}P NMR spectra gave no signals for either compound. A possible explanation for the lack of useful data obtained when characterising the sample using NMR could be due to paramagnetism caused by an unpaired electron in the nickel atom. The elemental analysis data was not presented here due to the large difference between calculated and experimental carbon, hydrogen and nitrogen values. This could be due to decomposition of the sample to a phosphine oxide and/or weakly complexed metal ions detaching from the ligand over time. The authors concluded that the crystal structure and mass spectrometry data were sufficiently accurate characterisation techniques to confirm the identity of each compound and that the crystal structures were by far the most important data required to illustrate the ring twisting capability required for preparation of compounds **(7)** and **(8)**.

By comparison, *ortho*lithiation of **(2)** and subsequent reaction with *N,N′*-dimethylaminodimethylchlorosilane using the same

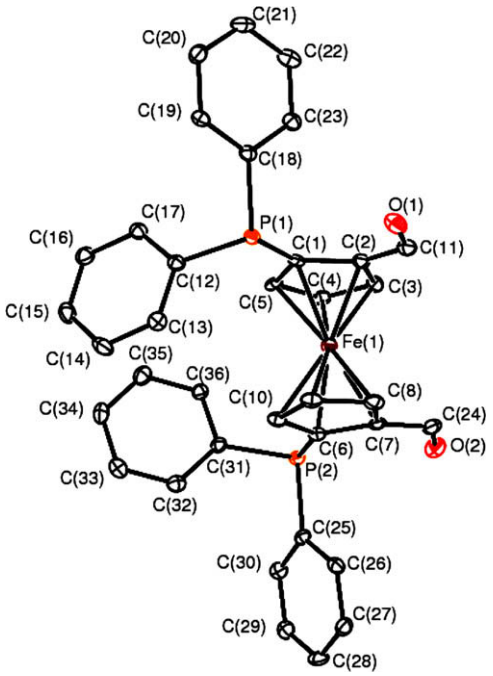


Fig. 3. Molecular structure of **(4)**.

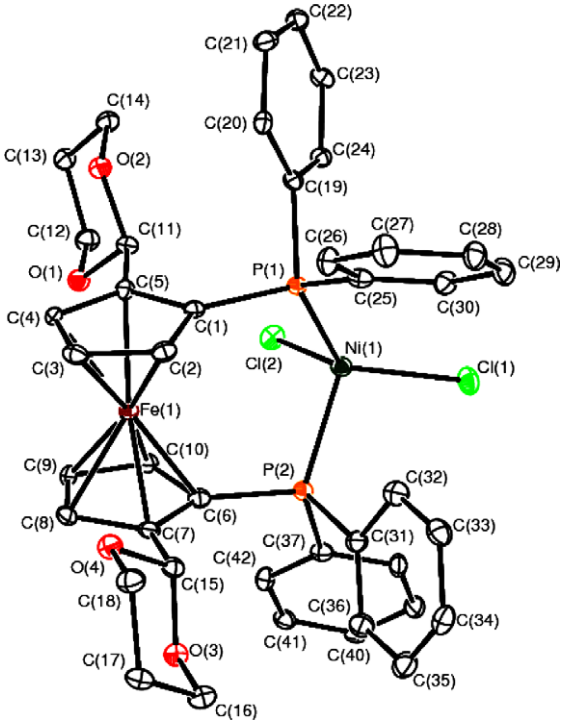


Fig. 4. Molecular structure of **(5)**.

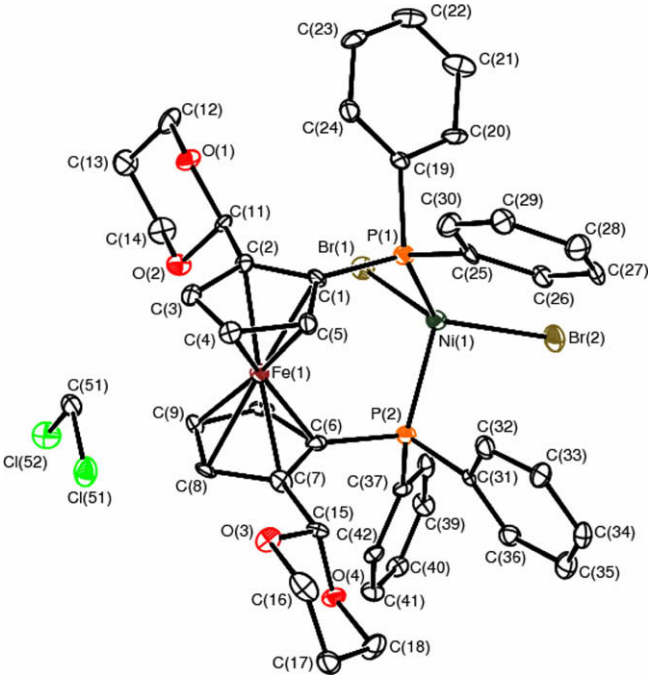


Fig. 5. Molecular structure of **(6)**.

conditions as for the synthesis of **(5)** gives the siloxane-bridged bisacetal ferrocenophane **(7)**, which X-ray crystallography again shows exhibits C_2 symmetry (Fig. 6), therefore the nature of the electrophile did not change the diastereoselectivity of the product and a chiral product, **(7)**, was obtained as a racemic mixture. The consistent orientation of the bridged products **(3)** and **(6)** is good evidence for the regioselective nature of this 1,1′ ortholithiation reaction. Finally, the siloxane-bridged acetal was deprotected under mildly acidic conditions to give the corresponding aldehyde

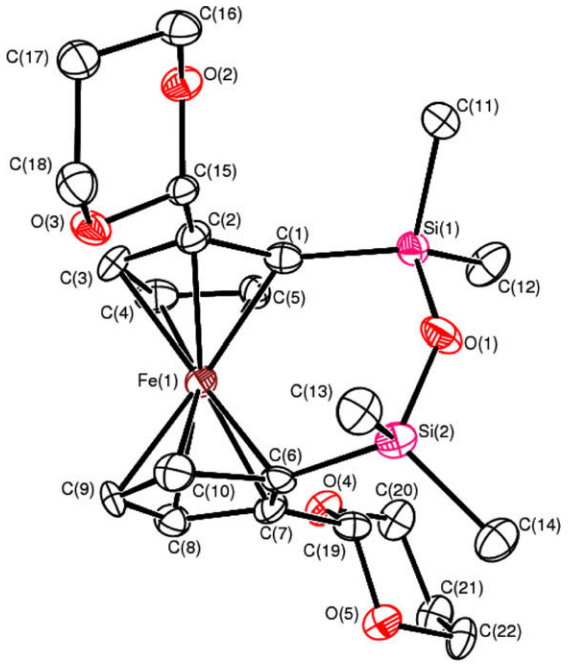


Fig. 6. Molecular structure of **(7)**.

(8). The aldehyde group appeared at 9.88 ppm in the ^{1}H NMR and at 192.86 ppm in the ^{13}C NMR. In addition, resonances from the acetal protecting group were no longer present in either spectrum. Finally, the molecular ion of **(8)** was detected using mass spectrometry and a crystal structure was obtained to confirm the identity of the sample (Fig. 7). A final dehydration step should yield 1,1′-siloxane-2,5′-bisethynylferrocene with acetylene groups in fixed position to prevent intramolecular coupling.

Silicon-ferrocenophanes such as 1,1,3,3-tetramethyl-1,3-disila-2-oxa[3]ferrocenophane are of interest in polymerisation reactions [33–35]. This particular ferrocenophane is related to **(7)** and **(8)** but without the additional 2,5′-substitution we report here. Previous methods to make 1,1,3,3-tetramethyl-1,3-disila-2-oxa[3]ferrocenophane have involved the solvolysis of precursors such as 1,1′-bis(chlorodimethylsilane)ferrocene [36], 1,1′-bis(dimethylsilane)ferrocene [37] or Fe(η^5-$C_5H_4SiMe_2XEt)_2$ (where X = O [37] or N [38]. However, Keppler et al. have reported an improved synthesis and a new crystal structure for 1,1,3,3-tetramethyl-1,3-disila-2-oxa[3]ferrocenophane from 1,1′-dilithioferrocene · TMEDA and dichlorodimethylsilane in a one-pot reaction [39]. Our method to produce the siloxane bridge of the ferrocenophane is similar to that of Keppler et al. in that it is a one-pot reaction, but here we used *N,N*′-dimethylaminodimethylchlorosilane rather than dichlorodimethylsilane, obtaining a similar yield of 61% compared to the 58% previously reported.

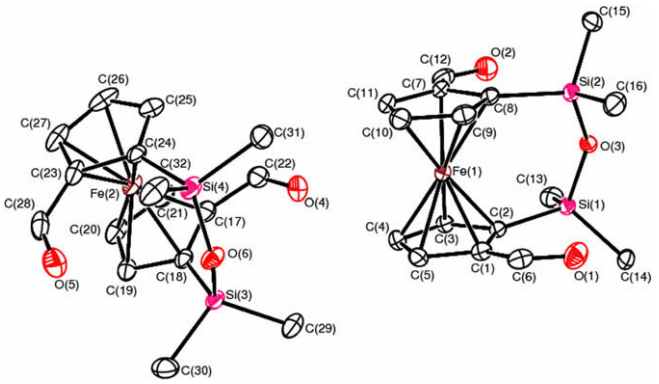


Fig. 7. Molecular structure of **(8)**. Both crystallographically independent molecules are shown.

3. Conclusion

The reaction of **(2)** with 2.2 equivalents of *tert*-butyllithium followed by 2.2 equivalents of a phosphine electrophile results in formation of *ortho*substituted 2,2′-bis(acetal)-1,1′- diphenylphosphinoferrocene. Complexation of this to a nickel halide effectively ring locks the Cp rings of the ferrocene, creating a 1,1′-diphosphino-2,5′-bis(acetal) arrangement. A similar lithiation followed by treatment with a silane electrophile directly yields *ortho*-substituted 1,1′-siloxane-2,5′-bis(acetal)ferrocene. Thus, these reaction conditions and this acetal group consistently provide chiral C_2-symmetric products (as racemic mixtures). The diastereoselectivity in the product results from a regioselectivity which can be used to synthesize ring-locked ferrocenes with the functional groups oriented on opposite sides of the ring lock on the top and bottom Cp rings. Hence, this acetal is an alternative protecting group to aminoalkoxides for the regioselective synthesis of 1,1′,2,2′-tetrasubstituted ferrocenes. In addition, deprotection of the acetal groups successfully yields aldehydes.

4. Experimental

4.1. General procedures

All experiments were conducted under a dry nitrogen or argon atmosphere using standard oven-dried Schlenk glassware, unless otherwise indicated. NMR spectra were recorded on a Bruker AC500 instrument operating at 500 MHz for ^{1}H, 125 MHz for ^{13}C and 202.5 MHz for ^{31}P. Chemical shifts (δ) are given in ppm and are relative to tetramethylsilane (for ^{1}H and ^{13}C) and triphenylphosphine (for ^{31}P). *J* values are given in Hz and refer to $J_{H,H}$ unless otherwise indicated. Mass spectra were recorded using electron impact, chemical ionisation (NH_3), fast atom bombardment, electrospray, matrix-assisted laser desorption ionisation and laser desorption ionisation at the EPSRC National Mass Spectrometry Service at the University of Swansea. Infrared spectra were recorded on a Perkin–Elmer 1600 series FTIR spectrometer. Elemental analysis was performed on a Carlo Erba EA1108 elemental analyser. All dry solvents were purchased as anhydrous solvents except THF which was dried using sodium wire.

4.2. X-ray crystallography

Compounds **(2)** and **(8)**: Suitable crystals were selected and datasets were measured on a Bruker APEXII CCD diffractometer at Station 9.8 of the Daresbury Synchrotron Radiation Source (**(2)**: λ = 0.6710 Å, **(8)**: λ = 0.6893 Å) at 120 K, because of the very weak diffraction observed for these small crystals. The data collections were driven by the Bruker APEX2 software [40] and processed by SAINT [41]. Absorption corrections were applied using SADABS [42]. The structures were solved and refined by a full-matrix least-squares procedure on F^2 in the Bruker SHELXTL software suite [43].

Compounds **(3)**–**(7)**: Suitable crystals were selected and datasets for **(3)** and **(7)** were measured on a Bruker APEXII CCD diffractometer and for **(4)**–**(6)** on a Bruker-Nonius KappaCCD diffractometer, both at the windows of a Bruker-Nonius FR591 rotating anode ($\lambda_{Mo\ K\alpha}$ = 0.71073 Å) at 120 K. The data collections were driven by COLLECT [44] and processed by DENZO [45]. Absorption corrections were applied using SADABS [42]. The

structures of **(3)**, **(4)** and **(7)** were solved in SIR2004 [46] and those of **(5)** and **(6)** were solved in SHELXS97 [43]; all five structures were refined by a full-matrix least-squares procedure on F^2 in SHELXL97 [43].

For all structures **(2)**–**(8)** all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters scaled to the equivalent isotropic displacement parameter (U_{eq}) of the parent atom. Tables 1–4 give crystal data, refinement information, and selected molecular geometry parameters.

Compound **(4)**: No obvious reason can be found in the data for the high R_{int} value and it is suggested that it is due to pseudo-symmetry in the unit cell parameters, possibly with unresolved twinning. The structure itself has been modelled satisfactorily.

Compound **(6)**: The R_{int} is very high and the value of R (observed reflections) is just over 0.1. The structure itself has been modelled satisfactorily. The crystal was a fine needle and the diffracted intensity was weak, leading to a low ratio of observed/unique reflections. In addition, the shape of the crystal and the highly absorbing nature of the compound made the process of correcting for absorption difficult. We feel that these are adequate explanations for the poor merging and refinement statistics.

Compound **(7)**: The dataset is composed of two diffraction patterns which are related by a 7.8° rotation. Attempts were made to de-convolute the two reciprocal lattices but there were not enough

Table 1
Crystal data and structural refinement for compounds **2**, **3**, **4**, **5** and **6**.

	2	**3**	**4**	**5**	**6**
	ssg0833	**2007src0239**	**2007src0411**	**2006src1354 (ACXT2)**	**2006src1355/ACXT1**
Formula	$C_{18}H_{22}FeO_4$	$C_{42}H_{40}FeO_4P_2$ 0.75CH_2Cl_2	$C_{36}H_{28}FeO_2P_2$	$C_{42}H_{40}Cl_2FeNiO_4P_2$	$C_{42}H_{40}Br_2FeNiO_4P_2$ CH_2Cl_2
Formula weight	358.21	790.22	610.37	856.14	1029.99
Temperature (K)	120	120	120	120	120
Wavelength (Å)	Synchrotron, 0.6710	0.71073	0.71073	0.71073	0.71073
Crystal colour and habit	Yellow plate	Yellow slab	Orange plate	Black slab	Green needle
Crystal size (mm)	0.04 × 0.02 × 0.01	0.14 × 0.09 × 0.04	0.22 × 0.12 × 0.01	0.28 × 0.20 × 0.10	0.46 × 0.03 × 0.02
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$Pbca$	$P\bar{1}$	$P2_1/c$
a (Å)	5.9067(18)	13.5058(7)	18.8060(7)	9.4907(5)	22.6916(11)
b (Å)	27.635(9)	11.0080(4)	15.7812(7)	10.5668(4)	9.3444(4)
c (Å)	9.645(3)	25.7852(12)	18.9241(9)	21.0227(11)	20.5597(10)
α (°)	90	90	90	76.361(3)	90
β (°)	93.303(4)	97.013(2)	90	89.822(3)	109.871(2)
γ (°)	90	90	90	64.009(3)	90
V (Å^3)	1571.8(9)	3804.9(3)	5616.3(4)	1829.46(15)	4099.9(3)
Z	4	4	8	2	4
θ range (°)	2.78–23.54	2.98–25.03	3.00–27.48	2.95–27.49	2.92–27.48
Reflections collected/unique	11,598/2761	30,788/6547	48,635/6443	32,185/8189	43,976/9380
R_{int}	0.0737	0.0941	0.1959	0.0954	0.2396
Observed reflections ($F^2 > 2\sigma$)	1971	4586	3723	5754	4077
Data/restraints/parameters	2761/0/209	6547/0/469	6443/0/370	8189/24/469	9380/0/497
Goodness of fit (F^2)	1.030	1.110	1.028	1.086	1.025
R, (obs) R_w (all data)	0.0475, 0.1188	0.0985, 0.2282	0.0753, 0.1403	0.0900, 0.2566	0.1071, 0.1762
Largest diff. peak and hole (e Å^{-3})	0.60, −0.55	1.18, −0.58	0.58, −0.46	1.20, −0.78	1.01, −0.85

Table 2
Selected bond lengths (Å) and angles (°) for (**2**), (**3**), (**4**), (**5**) and (**6**).

2		**3**		**4**		**5**		**6**	
C(1)–C(11)	1.481 (5)	C(1)–P(1)	1.815 (8)	C(1)–P(1)	1.830 (4)	C(1)–P(1)	1.814 (8)	C(1)–P(1)	1.810 (8)
C(11)–O(1)	1.399 (4)	P(1)–C(11)	1.849 (8)	P(1)–C(12)	1.831 (4)	P(1)–C(19)	1.825 (8)	P(1)–C(19)	1.808 (9)
C(11)–O(2)	1.423 (4)	P(1)–C(17)	1.831 (8)	P(1)–C(18)	1.838 (4)	P(1)–C(25)	1.819 (9)	P(1)–C(25)	1.831 (9)
O(1)–C(12)	1.443 (5)	C(2)–C(23)	1.510 (11)	C(2)–C(11)	1.458 (6)	C(5)–C(11)	1.481 (11)	C(2)–C(11)	1.479 (11)
O(2)–C(14)	1.429 (5)	C(6)–P(2)	1.815 (8)	C(11)–O(1)	1.211 (5)	C(6)–P(2)	1.791 (9)	C(6)–P(2)	1.805 (9)
C(6)–C(15)	1.497 (5)	P(2)–C(27)	1.839 (8)	C(6)–P(2)	1.834 (4)	P(2)–C(31)	1.804 (9)	P(2)–C(31)	1.812 (9)
C(15)–O(3)	1.382 (5)	P(2)–C(33)	1.845 (8)	P(2)–C(25)	1.837 (4)	P(2)–C(37)	1.830 (8)	P(2)–C(37)	1.812 (9)
C(15)–O(4)	1.389 (5)	C(7)–C(39)	1.504 (11)	P(2)–C(31)	1.840 (5)	C(7)–C(15)	1.482 (11)	C(7)–C(15)	1.494 (11)
O(3)–C(16)	1.446 (6)			C(7)–C(24)	1.458 (6)	Ni(1)–P(1)	2.321 (2)	Ni(1)–P(1)	2.353 (3)
O(4)–C(18)	1.446 (6)			C(24)–O(2)	1.216 (5)	Ni(1)–P(2)	2.301 (2)	Ni(1)–P(2)	2.311 (3)
C(1)–C(11)–O(1)	108.0 (3)	C(1)–P(1)–C(11)	99.7 (3)	C(1)–P(1)–C(12)	98.8 (2)	Ni(1)–Cl(1)	2.197 (2)	Ni(1)–Br(1)	2.346 (2)
C(1)–C(11)–O(2)	107.9 (3)	C(1)–P(1)–C(17)	103.8 (3)	C(1)–P(1)–C(18)	101.0 (2)	Ni(1)–Cl(2)	2.198 (2)	Ni(1)–Br(2)	2.349 (2)
C(11)–O(1)–C(12)	112.6 (3)	C(2)–C(23)–O(1)	109.4 (6)	C(2)–C(11)–O(1)	124.2 (5)	C(1)–P(1)–C(19)	104.3 (4)	C(1)–P(1)–C(19)	106.7 (4)
C(11)–O(2)–C(14)	110.9 (3)	C(2)–C(23)–O(2)	104.7 (6)	C(6)–P(2)–C(25)	100.5 (2)	C(1)–P(1)–C(25)	106.8 (4)	C(1)–P(1)–C(25)	103.6 (4)
C(6)–C(15)–O(3)	109.1 (3)	C(6)–P(2)–C(27)	104.5 (4)	C(6)–P(2)–C(31)	99.3 (2)	C(5)–C(11)–O(1)	110.2 (7)	C(2)–C(11)–O(1)	107.2 (7)
C(6)–C(15)–O(4)	110.2 (3)	C(6)–P(2)–C(33)	99.6 (3)	C(7)–C(24)–O(2)	124.8 (4)	C(5)–C(11)–O(2)	106.3 (6)	C(2)–C(11)–O(2)	109.5 (7)
C(15)–O(3)–C(16)	109.6 (4)	C(7)–C(39)–O(3)	106.3 (6)			C(6)–P(2)–C(31)	108.6 (4)	C(6)–P(2)–C(31)	109.9 (4)
C(15)–O(4)–C(18)	110.4 (4)	C(7)–C(39)–O(4)	108.7 (6)			C(6)–P(2)–C(37)	106.1 (4)	C(6)–P(2)–C(37)	102.2 (4)
						C(7)–C(15)–O(3)	108.9 (6)	C(7)–C(15)–O(3)	108.2 (7)
						C(7)–C(15)–O(4)	108.0 (7)	C(7)–C(15)–O(4)	108.0 (7)
						C(1)–P(1)–Ni(1)	113.1 (3)	C(1)–P(1)–Ni(1)	116.8 (3)
						C(6)–P(2)–Ni(1)	112.7 (3)	C(6)–P(2)–Ni(1)	112.4 (3)
						P(1)–Ni(1)–P(2)	103.56 (8)	P(1)–Ni(1)–P(2)	103.2 (1)
						Cl(1)–Ni(1)–Cl(2)	124.9 (1)	Br(1)–Ni(1)–Br(2)	122.14 (6)

non-overlapped reflections to make this possible. Thus only the major component has been integrated, with the overlap with the second component leading to the high R_{int} value. Furthermore, the structure has been refined as a mixture of enantiomers of ratio 52:48.

4.3. Preparation of 1,1′-ferrocenecarboxaldehyde (**1**) [28]

To a solution of ferrocene (15.00 g, 81 mmol) in hexane (300 ml) was added tetramethylethylenediamine (TMEDA) (2.2 eq, 26.6 ml, 177 mmol) and the mixture was stirred for 5 min. To this suspension was added dropwise *n*-butyllithium (2.2 eq, 71 ml, 177 mmol). The mixture was stirred at room temperature overnight. The reaction was cooled to −78 °C and THF (150 ml) followed by anhydrous DMF (2.2 eq, 13.7 ml, 177 mmol) were added. The mixture was stirred at −78 °C for 15 min followed by 1.5 h stirring at room temperature. The reaction was quenched with brine (60 ml) and CH_2Cl_2 (50 ml) was added. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 ml). The combined organic phases were dried ($MgSO_4$) and the solvents removed *in vacuo*. Column chromatography (SiO_2, hexane-ether 4:1 followed by hexane-ether-ethyl acetate 4:1:0.1 gradually increasing the ether and ethyl acetate) gives 1,1′-ferrocenecarboxaldehyde as a bright red crystalline solid in the third fraction. Yield (16.07 g, 82%), ^{1}H NMR 9.96 (s, 2H, C*H*O), 4.89 (s, 4H, α-Cp-C*H*), 4.68 (s, 4H, β-Cp-C*H*); ^{13}C NMR 192.81 (2 × *C*HO), 80.34 (2 × *ipso* Cp-*C*), 74.18 (4 × α-Cp-*C*H), 70.87 (4 × β-Cp-*C*H); Anal. Calc. for $C_{12}H_{10}O_2Fe$: C, 59.56; H, 4.17. Found: C, 59.67; H, 4.29%.

4.4. Preparation of 1,1′-bisacetalferrocene (**2**)

To a solution of 1,1′-ferrocenecarboxaldehyde (10.00 g, 41 mmol) in benzene (450 ml) 1,3-propanediol (9.9 eq, 29.3 ml, 406 mmol) and *p*-toluenesulfonic acid (0.16 eq, 1.25 g, 6.6 mmol) were added. The solution was refluxed for 24 h over a Dean-Stark trap with the exclusion of light. After addition of deactivated silica gel (50 ml) (hexane + 10% NEt_3) the solvent was removed *in vacuo*. Column chromatography (SiO_2, hexane + 10% NEt_3) of the residue yielded 1,1′-bisacetalferrocene as a yellow powder in the first fraction. Yield (11.89 g, 81%); ^{1}H NMR 5.32 (s, 2H, acetal *tertiary* C*H*), 4.24 (brs, 4H, α-Cp-C*H*), 4.12 (dd, 4H, acetal C*H*$_2$, *J* = 4.5, 11 Hz), 4.07 (brs 4H, β-Cp-C*H*), 3.84 (t, 4H, acetal C*H*$_2$, *J* = 11 Hz), 2.05 (m, 2H, acetal C*H*$_2$), 1.40 (d, 2H, acetal C*H*$_2$, *J* = 13.5 Hz); ^{13}C NMR 100.46 (2 × acetal tertiary *C*H), 86.55 (2 × *ipso* Cp-*C*), 68.93 (4 × α-Cp-*C*H), 67.37 (4 × β-Cp-*C*H), 67.23 (4 × acetal O-*C*H$_2$), 25.84 (2 × acetal *C*H$_2$); I.R. (KBr) 3049, 2959, 2852, 1476, 1432, 1367, 1241, 1148, 1114, 1015, 989, 824, 696 cm^{-1}; MS (LSIMS): M^+ calculated = 357, M^+ found = 358, MS (ES +) *m*/*e* Accurate Mass

Table 3
Crystal data and structural refinement for compounds **7** and **8**.

	7	**8**
	2007src0319	**ssg1525**
Formula	$C_{22}H_{32}FeO_5Si_2$	$C_{16}H_{20}FeO_3Si_2$
Formula weight	488.51	372.35
Temperature (K)	120	120
Wavelength (Å)	0.71073	Synchrotron, 0.6893
Crystal colour and habit	Orange block	Orange plate
Crystal size (mm)	0.14 × 0.08 × 0.04	0.08 × 0.04 × 0.02
Crystal system	Orthorhombic	Triclinic
Space group	$Pna2_1$	$P\bar{1}$
a (Å)	19.4040(13)	7.9457(15)
b (Å)	8.8831(4)	14.656(3)
c (Å)	13.4774(9)	15.163(3)
α (°)	90	79.463(2)
β (°)	90	78.676(2)
γ (°)	90	89.908(2)
V (Å^3)	2323.1(2)	1701.1(6)
Z	4	4
θ range (°)	3.11–25.03	2.54–24.20
Reflections collected/unique	18,918/4035	12,503/5935
R_{int}	0.1383	0.0228
Observed reflections ($F^2 > 2\sigma$)	2947	5054
Data/restraints/parameters	4035/1/276	5935/0/397
Goodness of fit (F^2)	1.079	1.060
R, (obs) R_w (all data)	0.0720, 0.1763	0.0558, 0.1580
Largest diff. peak and hole (e Å^{-3})	0.46, −0.48	1.38, −0.45

Table 4
Selected bond lengths (Å) and angles (°) for (**7**) and (**8**).

7		**8**			
		Molecule (a)		**Molecule (b)**	
C(1)–Si(1)	1.847 (10)	C(2)–Si(1)	1.873 (4)	C(18)–Si(3)	1.870(4)
Si(1)–O(1)	1.628 (13)	Si(1)–O(3)	1.637 (3)	Si(3)–O(6)	1.635 (3)
Si(1)–C(11)	1.875 (10)	Si(1)–C(13)	1.856 (5)	Si(3)–C(29)	1.853 (4)
Si(1)–C(12)	1.873 (11)	Si(1)–C(14)	1.854 (4)	Si(3)–C(30)	1.863 (5)
C(2)–C(15)	1.493 (11)	C(1)–C(6)	1.456 (6)	C(17)–C(22)	1.464 (7)
C(6)–Si(2)	1.886 (10)	C(6)–O(1)	1.218 (6)	C(22)–O(4)	1.212 (6)
Si(2)–O(1)	1.640 (13)	C(8)–Si(2)	1.877 (4)	C(24)–Si(4)	1.869 (4)
Si(2)–C(13)	1.844 (11)	Si(2)–O(3)	1.645 (3)	Si(4)–O(6)	1.643 (3)
Si(2)–C(14)	1.833 (11)	Si(2)–C(15)	1.854 (5)	Si(4)–C(31)	1.856 (5)
C(7)–C(19)	1.488 (11)	Si(2)–C(16)	1.859 (5)	Si(4)–C(32)	1.858 (5)
		C(7)–C(12)	1.450 (6)	C(23)–C(28)	1.446 (7)
		C(12)–O(2)	1.217 (6)	C(28)–O(5)	1.224 (6)
C(1)–Si(1)–O(1)	110.4 (4)	C(2)–Si(1)–O(3)	110.6 (2)	C(18)–Si(3)–O(6)	110.9 (2)
C(1)–Si(1)–C(11)	110.4 (4)	C(2)–Si(1)–C(13)	106.1 (2)	C(18)–Si(3)–C(29)	112.8 (2)
C(1)–Si(1)–C(12)	109.1 (5)	C(2)–Si(1)–C(14)	113.3 (2)	C(18)–Si(3)–C(30)	106.0 (2)
C(11)–Si(1)–C(12)	107.8 (6)	C(13)–Si(1)–C(14)	108.9 (2)	C(29)–Si(3)–C(30)	108.4 (2)
C(2)–C(15)–O(2)	108.7 (7)	C(1)–C(6)–O(1)	124.7 (4)	C(17)–C(22)–O(4)	125.1 (5)
C(2)–C(15)–O(3)	109.9 (6)	C(8)–Si(2)–O(3)	110.1 (2)	C(24)–Si(4)–O(6)	110.7 (2)
C(6)–Si(2)–O(1)	110.2 (4)	C(8)–Si(2)–C(15)	112.1 (2)	C(24)–Si(4)–C(31)	106.9 (2)
C(6)–Si(2)–C(13)	108.5 (5)	C(8)–Si(2)–C(16)	108.0 (2)	C(24)–Si(4)–C(32)	111.1 (2)
C(6)–Si(2)–C(14)	111.3 (5)	C(15)–Si(2)–C(16)	109.4 (2)	C(31)–Si(4)–C(32)	110.1 (3)
C(13)–Si(2)–C(14)	110.9 (5)	C(7)–C(12)–O(2)	125.2 (4)	C(23)–C(28)–O(5)	127.1 (4)
C(7)–C(19)–O(4)	109.4 (7)	Si(1)–O(3)–Si(2)	141.9 (2)	Si(3)–O(6)–Si(4)	141.5 (2)
C(7)–C(19)–O(5)	109.4 (7)				
Si(1)–O(1)–Si(2)	142.6 (3)				

Reference compound: Polyethylenimine $[M + H]^+$ Calculated = 359.0940, found = 359.0940.

4.5. Preparation of 2,2′-bis-(acetal)-1,1′-diphenylphosphinoferrocene (**3**)

To a cooled (−78 °C) solution of 1,1′-bisacetalferrocene (5.00 g, 14 mmol) in dry ether (250 ml) was added dropwise *tert*-butyllithium (2.2 eq, 1.7 M in pentane, 18.1 ml, 31 mmol). The mixture was stirred at −78 °C for 15 min and the cooling bath was removed and stirring continued at room temperature for 2 h. The reaction was cooled to −78 °C and chlorodiphenylphosphine (2.2 eq, 6.84 g, 31 mmol) was added. The mixture was stirred at −78 °C for 15 min followed by 1.5 h stirring at room temperature. The reaction was treated with water (60 ml) and CH_2Cl_2 (50 ml) was added. The phases were separated and the aqueous phase was extracted CH_2Cl_2 (3 × 30 ml). The combined organic phases were dried ($MgSO_4$) and the solvents removed *in vacuo*. The crude product was dissolved in dry ether and cooled to −20 °C. This resulted in crystallisation of 2,2′-bis-(acetal)-1,1′-diphenylphosphinoferrocene as a dark yellow solid. Yield (6.3 g, 62%); ^{1}H NMR 7.42–7.39 (m, 5H, Ar), 7.32–7.28 (m, 3H, Ar), 7.26–7.23 (m, 3H, Ar), 7.20–7.19 (m, 5H, Ar), 7.15–7.12 (m, 4H, Ar), 5.59 (d, 2H, acetal *tertiary* C*H*, *J* = 1.0 Hz), 4.73 (bs, 2H, α-Cp-C*H*), 4.22 (bs, 2H, acetal C*H*), 4.07 (bs, 2H, β-Cp-C*H*), 3.93 (bs 2 × C*H* acetal), 3.86 (d, 1H, acetal C*H*, *J* = 4.7 Hz), 3.83 (d, 1H, acetal C*H*, *J* = 4.7 Hz) 3.74 (bs, 2H, acetal C*H*), 3.31 (s, 2H, α′-Cp-C*H*), 1.97 (m, 2H, acetal C*H*), 1.27 (d, 2H, acetal C*H*, *J* = 13.2 Hz); ^{13}C NMR 140.22 (d, 2C, Ar-*C*P, J_{C-P} = 9.2 Hz), 137.61 (d, 2C, Ar-*C*P, J_{C-P} = 9.2 Hz), 135.07 (d, 4C, *meta* P-Ar-*C*H, J_{C-P} = 21.1 Hz), 132.32 (d, 4C, *meta* P-Ar-*C*H, J_{C-P} = 17.4 Hz), 129.02 (2C, *para* P-Ar-*C*H), 128.03 (d, 4C, *ortho* P-Ar-*C*H, J_{C-P} = 7.3 Hz), 127.56 (d, 4C, *ortho* P-Ar-*C*H, J_{C-P} = 5.5 Hz), 127.26 (2C, *para* P-Ar-*C*H), 99.43 (d, 2C, *tertiary* acetal C, J_{C-P} = 7.3 Hz), 92.82 (2C, Cp-*C*-P, J_{C-P} = 22.0 Hz), 75.47 (2C, Cp-*C*-acetal), 72.75 (d, 2C, α′-Cp-*C*H, J_{C-P} = 12.8 Hz), 72.42 (2C, α-Cp-*C*H), 72.31 (d, 2C, β-Cp-*C*H J_{C-P} = 3.7 Hz), 67.18 (d, 2C, acetal O-*C*H_2, J_{C-P} = 4.6 Hz), 66.71 (d, 2C, acetal O-*C*H_2, J_{C-P} = 2.8 Hz), 25.67 (2C, acetal *C*H_2); ^{31}P NMR −21.29 (P-Ar); I.R. (KBr) 3092, 2962, 2922, 2851, 1382, 1283, 1239, 1104, 1001, 812 cm^{-1}; MS (LSIMS): M^+ calculated = 726, M^+ found = 726.1, MS (ES +) *m*/*e* Accurate Mass Reference compound: Perfluorotributylamine; Calculated = 726.1746, found = 726.1752.

^{31}P NMR for oxidized phosphines 28.17 (O=*P*-Ar).

4.6. Preparation of 1,1′-bis-carboxaldehyde-2,2′-diphenylphosphinoferrocene (4)

To a solution of 1,1′-bis-(acetal)-2,2′-diphenylphosphinoferrocene (1.00 g, 1.4 mmol) in (THF) (20 ml) and water (*ca.* 1 ml) was added *p*-toluenesulfonic acid (1 eq, 0.260 g, 1.4 mmol). The mixture was stirred with the exclusion of light for 3 h. After 3 h, the organic phase was extracted using CH_2Cl_2 (30 ml) and the combined organic phases were dried over magnesium sulfate followed by removal of the solvent *in vacuo*. Column chromatography of the residue with ether (to remove 1,3-propanediol and other impurities) followed by CH_2Cl_2 gave 1,1′-bis-carboxaldehyde-2,2′-diphenylphosphinoferrocene in the second fraction as a red solid. Yield (0.720 g, 84%), ^{1}H NMR 10.05 (d, 2 × C*H*O, J_{P-H} = 2.2 Hz), 7.31–7.28 (m, 6H, Ar), 7.21–7.15 (m, 8H, Ar), 7.04–7.01 (pseudo t, 6H, Ar) 5.15 (bs, 2H, α(CHO)-Cp-C*H*), 4.65 (pseudo t, 2H, β-Cp-C*H*, *J* = 4.7 Hz), 3.63 (bs, 2H, α′(PPh_2)-Cp-C*H*); ^{13}C NMR 192.49 (d, 2C, *C*HO, J_{C-P} = 9.2 Hz), 135.54 (d, 4C × Ar-*C*P, J_{C-P} = 11.0 Hz), 134.66 (d, 4C, *meta* P-Ar-*C*H, J_{C-P} = 21.1 Hz), 132.15 (d, 4C, *meta* P-Ar-*C*H, J_{C-P} = 19.3 Hz), 129.75 (4C, *para* P-Ar-*C*H), 128.48 (m, 8C, *ortho* P-Ar-*C*H), 84.68 (2C, Cp-*C*-P-Ar), 84.58 (2C, Cp-*C*-CHO), 82.54 (2C, α-Cp-*C*H), 77.69 (2C, β-Cp-*C*H), 75.20 (2C, α′-Cp-*C*H); ^{31}P NMR -24.05 (P-Ar); I.R. (KBr) 3054, 2818, 2794, 2774, 2744, 1682, 1478, 1432, 1361, 1249, 1163, 1089, 1069, 1040, 1026, 999, 842, 695 cm^{-1}; MS (LSIMS): M^+ calculated = 610, M^+ found = 610, MS (ES +) *m*/*e* Accurate Mass Reference compound: Perfluorotributylamine Calculated = 610.0908, found = 610.0912.

^{31}P NMR for oxidized phosphines 25.17 (O=*P*-Ar).

4.7. Preparation of the nickel(II) chloride complex of 1,1′-bis-(acetal)-2,2′- diphenylphosphinoferrocene (**5**)

To a solution of $NiCl_2(DME)_2$ (0.094 g, 3.3 mmol) in anhydrous CH_2Cl_2 (*ca.* 2 ml) was added 1,1′-bis-(acetal)-2,2′-diphenylphosphinoferrocene (0.45 eq, 0.110 g, 1.52 mmol). The solution was layered with anhydrous ether and stored in the dark under nitrogen. After *ca.* 72 h, dark green crystals of the nickel chloride complex were filtered off from a dark green opaque solution. The crystals were washed with petrol and ether and stored in the dark under nitrogen. Yield (0.55 g, 42%), MS (EI +): M^+ calculated = 854.7, M^+ found = 726.1, MS (EI +) *m*/*e* Accurate Mass Reference compound: Perfluorotributylamine, Calculated = 854.7, found = 726.1749. *Note*: mass spectrometry of (**5**) showed only a clean molecular ion of (*m*/*z* = 726.1749) which corresponds to the uncomplexed diphosphinoferrocene (**3**) in EI and FAB modes implying a weakly-bound complex for (**5**). *Note:* NMR is not reported due to the lack of useful data caused by paramagnetism due to an unpaired electron in the nickel atom. The elemental analysis shows a large difference between calculated and experimental carbon, hydrogen and nitrogen values and has therefore not been reported here. This could be due to decomposition of the sample to a phosphine oxide and/or weakly complexed metal ions detaching from the ligand over time.

4.8. Preparation of the nickel(II) bromide complex of 1,1′-bis-(acetal)-2,2′-diphenylphosphinoferrocene (**6**)

To a solution of $NiBr_2(DME)_2$ (0.122 g, 3.3 mmol) in anhydrous CH_2Cl_2 (*ca.* 2 ml) was added 1,1′-bisacetal-2,2′-diphenylphosphinoferrocene (0.45 eq, 0.110 g, 1.52 mmol). The solution was layered with anhydrous ether and stored in the dark under nitrogen. After *ca.* 72 h, dark green crystals of the nickel bromide complex were filtered off from a dark green opaque solution. The crystals were washed with petrol and ether and stored in the dark under nitrogen. Yield (0.56 g, 39%), MS (LSIMS): M^+ calculated = 944, M^+ found = 943, MS (ES +) *m*/*e* Accurate Mass Reference compound: Perfluorotributylamine Calculated = 941.9466, found = 941.9462. *Note:* NMR and elemental analysis data have not been reported for compound (**6**) due to the same reasons as those given above for (**5**).

4.9. Preparation of 1,1′-siloxane-2,5′-bisacetalferrocenophane (**7**)

To a cooled (−78 °C) solution of 1,1′-bisacetalferrocene (1.00 g, 2.8 mmol) in dry ether (75 ml) *tert*-butyllithium (2.2 eq, 1.7 M in pentane, 3.6 ml, 6.2 mmol) was added. The mixture was stirred at −78 °C for 15 min; the cooling bath was removed and stirring continued at room temperature for 2 h. The reaction was cooled to −78 °C and *N*,*N*′-dimethylaminodimethylchlorosilane (1.04 g, 8.4 mmol) was added; the mixture was stirred at −78 °C for 15 min followed by 1.5 h stirring at room temperature. The reaction was quenched with water (60 ml) and diethyl ether (50 ml) was added. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 ml). The combined organic phases were dried ($MgSO_4$) and the solvents removed *in vacuo*. 1,1′-Siloxane-2,5′-bisacetalferrocenophane **(7)** was obtained as orange crystals after recrystallisation from *n*-hexane. Yield (0.83 g, 61%) ^{1}H NMR 5.28 (s, 2H, acetal *tertiary* C*H*), 4.54 (ps, 2H, α-Cp-

C*H*), 4.41 (ps, 2H, α′-Cp-C*H*), 4.25 (m, 2H, acetal C*H*), 4.23 (ps, 2H, β-Cp-C*H*) 4.17 (bs, 2H, acetal C*H*), 3.90 (m, 4H, acetal C*H*), 2.18 (m, 2H, acetal C*H*), 1.40 (d, 2H, acetal C*H*, J = 13.6 Hz), 0.37 (s, 6H, methyl C*H*), 0.32 (s, 6H, methyl C*H*); ^{13}C NMR 99.66 (2C, acetal *tertiary* C), 89.87 (2C, *ipso*-Cp-*C*-acetal), 77.91 (2C, α-Cp-*C*H), 70.27 (2C, β-Cp-*C*H), 69.40 (2C, α′-Cp-*C*H), 68.80 (2C, *ipso* Cp-*C*-Siloxane), 66.20 (4C, acetal O-*C*H$_2$), 39.77 (2C, acetal O-*C*H$_2$), 25.84 (2C, acetal *C*H$_2$), 0.35 (2C, Si-*C*H$_3$), 0.00 (2C, Si-*C*H$_3$); IR (KBr) 3081, 2958, 2925, 2843, 2721, 1469, 1455, 1393, 1378, 1364, 1273, 1251, 1146, 1106, 1078, 1019, 995, 826, 692 cm^{-1}; MS (LSIMS): M$^+$ calculated = 488, M$^+$ found = 488.1, MS (ES +) *m*/*e* Accurate Mass Reference compound: Polyethylenimine [M + H]$^+$ Calculated = 487.1257, found = 487.1258.

*4.10. Preparation of 1,1′-siloxane-2,5′-ferrocenophanecarboxaldehyde (**8**)*

To a solution of 1,1′-siloxane-2,5′-bisacetalferrocenophane (0.06 g, 0.123 mmol) in THF (20 ml) and water (*ca.*1 ml) was added *p*-toluenesulfonic acid (1 eq, 0.07 g, 0.37 mmol). The mixture was stirred with the exclusion of light for 3 h. After 3 h, the organic phase was extracted using CH_2Cl_2 (30 ml), and the combined organic phases were dried over magnesium sulfate followed by removal of the solvent *in vacuo*. 1,1′-Siloxane-2,5′-ferrocenophanecarboxaldehyde was recrystallised from diethyl ether layered with hexane to give red crystals. Yield (0.035 g, 80%), ^{1}H NMR 9.88 (s, 2H, C*H*O), 4.73 (bs, 2H, α-Cp-C*H*), 4.68 (brs 2H, α′-Cp-C*H*,), 4.44 (brs 2H, β-Cp-C*H*), 0.26 (s, 6H, methyl C*H*), 0.17 (s, 6H, methyl C*H*); ^{13}C NMR 192.86 (s, 2C, *C*HO), 83.50 (2C, Cp-*C*-CHO), 82.67 (2C, α-Cp-*C*H), 75.44 (2C, β-Cp-*C*H), 74.89 (2C, α′-Cp-*C*H), 73.71 (2C, Cp-*C*-Siloxane) 0.74 (2C, Si-*C*H$_3$), 0.00 (2C, Si-*C*H$_3$); MS (LSIMS): M$^+$ calculated = 356, M$^+$ found = 357.

Acknowledgements

The authors sincerely thank the EPSRC, Corus Colors Ltd and the EPSRC EngD Scheme in Steel Technology at Swansea University for financial support for AC, the EPSRC National Mass Spectrometry Service at Swansea for MS data, the EPSRC for funding of the National Crystallography Service, and STFC for access to synchrotron facilities.

Appendix A. Supplementary material

CCDC 695609–695615 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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