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The synthesis of chiral ferrocene ligands and their metal complexes

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Abstract

Starting from the well known N,N-dimethylaminoethylferrocene (**1**) {or N,N-dimethyl(1-ferrocenylethyl)amine}, further substitution of the cyclopentadienyl ring in an adjacent position enables formation of -iodo (**2**), -trimethylsilylethynyl (**3**) and -ethynyl (**4**) derivatives in good yields. From **4**, *fac*-[manganese1,2-bis(diphenylphosphinomethane)(tricarbonyl)acetylide] (**5**), *trans*-[rutheniumdi(1,2-bis(diphenylphosphinomethane))chloro-acetylide] (**6**) and *trans*-[osmiumdi(1,2-bis(diphenylphosphinomethane))chloro-acetylide] (**7**) have been synthesised and characterised. Electrochemical experiments in solution indicate that there is a decrease in polarisation and a decrease in the degree of metal-to-metal interaction in the chiral ferrocenyl metal-acetylides as opposed to the non-chiral analogues. Second harmonic generation (Kurtz powder) measurements are reported on the chiral metal complexes, but unfortunately negligible second-order non-linear activity was observed.

1. Introduction

The field of metallocene chemistry has recently undergone something of a renaissance, primarily due to the rapid growth of material science [1]. Of the enormous number of derivatives formed, chiral ferrocene species have proved to be of particular interest in two fields. Firstly, in the development of ferrocene derivatives exhibiting large second harmonic generation (SHG) efficiencies where the material needs to crystallise in a non-centrosymmetric space group [2]. Chiral, enantiomerically pure ferrocene compounds can go some way to ensuring the required crystallisation, and aid the potential NLO properties [3]. Secondly, the use of chiral metal catalysts in asymmetric and enantiomeric syntheses is now a mature science. Optically active, ferrocenyl phosphines have proved to be effective as chiral ligands for asymmetric reactions catalysed by transition metal complexes due to the presence of a stereogenic, functionalised side chain which can be modelled to fulfill specific purposes [4]. Chiral ferrocenyl alcohols have been used in stereoselective peptide syntheses [5], and chiral diferrocenyl dichalcogenides are important in the rhodium-catalysed asymmetric hydrosilylation of alkyl aryl ketones [6].

We can now report the synthesis and characterisation of a series of chiral, dimethylaminoethyl ferrocene complexes and their manganese-, ruthenium- and osmium-acetylide derivatives, all of which are of interest to both of the above areas.

2. Results and discussion

2.1. Synthesis

Starting from the well-known N,N-dimethylaminoethylferrocene [7], further selective substitution of the cyclopentadienyl ring [8] in an adjacent position enables the formation of -iodo (**2**), -trimethylsilylethynyl (**3**) and -ethynyl (**4**) derivatives in good yields. The retrosynthesis of the compounds from the chiral ethynylferrocene ligand (**4**) is described in Scheme 1. The starting material (**1**) was synthesised by a literature method [7], in yields comparable with those reported. The racemic mixture was then resolved into its (R)-

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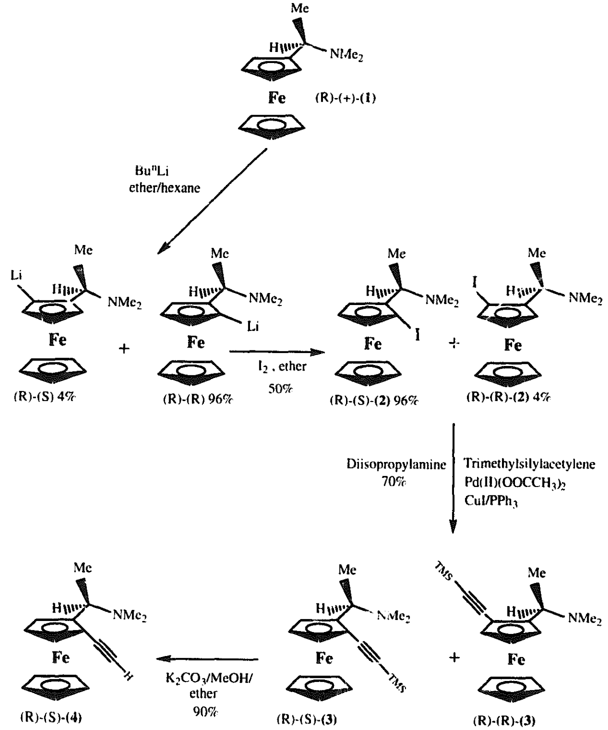
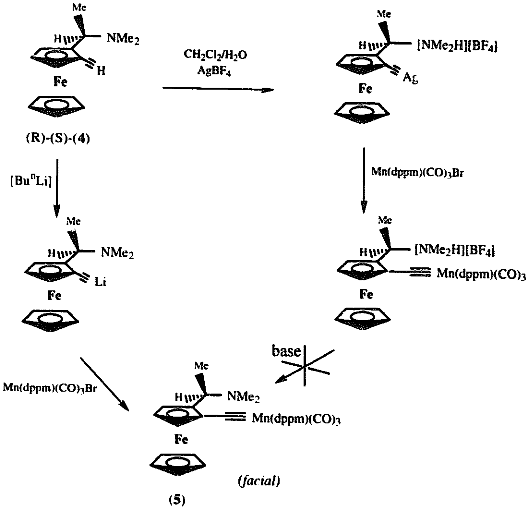


Scheme 1. Synthesis of chiral ferrocenyl-acetylide ligands.

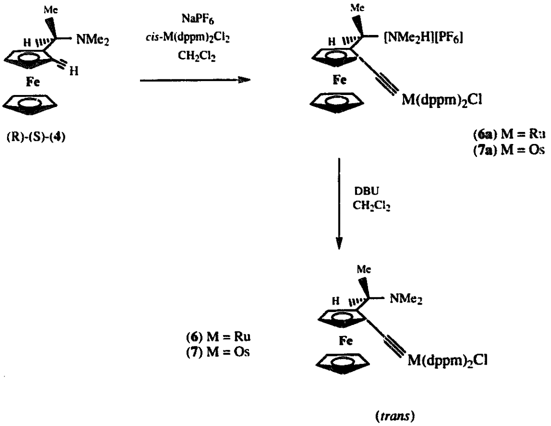
(+)-(1) and (S)-(−)-(1) enantiomers by a modified literature procedure [9]. Taking the (R)-(+)- enantiomer, a 96% to 4% diastereoisomeric mixture {(R)-(R)/(R)-(S)} of the lithio complex could be formed by stereoselective lithiation following addition of a slight excess of *n*-BuLi in hexanes at room temperature [9]. Subsequent iodination of this reactive intermediate was accomplished in situ by adding a solution of iodine in diethylether via a cannular at −78 °C. The mixture was stirred for 1 h at this temperature before being allowed to warm to room temperature. Removal of the solvent resulted in the isolation of the diastereoisomeric products {96:4 of (R)-(S)-(2):(R)-(R)-(2)} as an orange oil in ca. 50% yield. The iodo diastereoisomers could not be separated at this stage, so the mixture was further manipulated via a coupling reaction of the iodo group with trimethylsilylacetylene. This type of reaction has been utilised extensively within our group and general experimental details can be found elsewhere [10,11]. This gave a 96:4 mixture of (R)-(S)-(3):(R)-(R)-(3), which could be separated by repeated column chromatography using neutral grade II alumina and diethylether as eluent to yield, upon removal of solvent, the pure diastereoisomer (R)-(S)-(3) as a dark orange solid in ca. 70% yield. The desilylation of complex (R)-(S)-(3) was carried out by the action of a methanol/diethylether/K_2CO_3 solution. Complex (R)-(S)-(4), an orange crystalline material, was isolated in 95% yield without further purification being required. The (S) isomer can be manipulated in a similar way to finally give the analogous (S)-(R)-(4) species in equivalent yields.

The chiral ethynylferrocene {(R)-(S)-(4)} was reacted with the complex [Mn(dppm)(CO)$_3$Br] (dppm = 1,2-bis(diphenylphosphino)methane), in an attempt to form



Scheme 2. Synthetic routes to chiral ferrocenyl-manganese complexes.

the chiral *facial*-ferrocenyl metal-acetylide (**5**). The initial synthetic route was similar to that used in the previously described ferrocenyl manganese-acetylides [12,13]. This method only gave a 50:50 mixture (as monitored by IR spectroscopy) of starting material and product, which could not be separated from each other.



Scheme 3. Synthesis of chiral ferrocenyl-ruthenium and -osmium complexes.

Attempts to increase the reaction yield using excess ligand were unsuccessful. The reaction should proceed via the formation of a silver acetylide complex, which should then attack the metal chloride bond giving the required metal-acetylide and silver chloride as products. It is predicted that the HBF_4 by-product of the silver acetylide formation can protonate the tertiary amine, giving a charged complex (Scheme 2). Formation of this charged species prevents completion of the reaction and the charge on the complex hinders separation by column chromatography. Attempts to remove the proton on the tertiary amine with a base before purification led to decomposition of the product, which was also the result of attempted purification of the charged complex by recrystallisation.

An alternative synthesis of the chiral ferrocenylmanganese complex (**5**) was therefore utilised and featured the reaction of equimolar amounts of the lithium-acetylide derivative and $[Mn(dppm)(CO)_3Br]$. The reaction was carried out in THF at room temperature and IR spectroscopy indicated that the reaction was only 50% complete. Attempts to increase this yield by variation of temperature, solvent and reactant stoichiometry were unsuccessful, but as the amine functional group was no longer protonated, **5** could be isolated by column chromatography as an orange powder.

The synthesis of chiral ferrocenyl metal-acetylides via the same methods used to isolate the non-chiral *trans*-ferrocenyl-ruthenium and -osmium complexes [14] gave lower than expected yields. The reaction of the non-chiral ethynylferrocene with the *cis*-metal precursors ($[Ru(dppm)_2Cl_2]$ M = Ru or Os) resulted in the formation of the vinylidene complexes with IR stretching frequencies ca. $1653\,cm^{-1}$. These were converted in situ to the ferrocenylacetylides (**10**) and (**11**) (IR $\nu(C{\equiv}C)$ ca. $2084\,cm^{-1}$) by addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [14,15].

The reaction of the chiral ethynylferrocene {(R)-(S)-(**4**)} appeared to proceed directly to the ferrocenyl metal-acetylide complexes ($\nu(C{\equiv}C)$ $2084\,cm^{-1}$), without addition of DBU. It is postulated that the amine functional group in **4** acts as a base in the reaction mixture, and any vinylidene intermediate formed undergoes an intermolecular or intramolecular proton transfer to the amine group on the chiral ethynylferrocene, allowing the acetylides to be formed without addition of a base (Scheme 3).

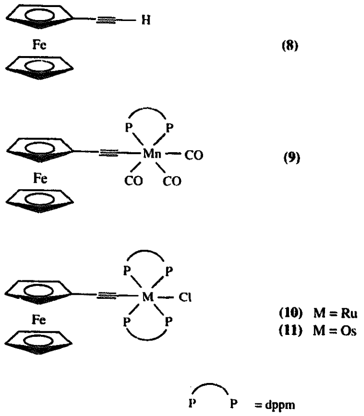
These acetylide complexes (**6a**) and (**7a**) have the same $\nu(C{\equiv}C)$ stretching frequencies as the non-chiral analogues, but contain a charged ammonium salt on the ferrocene ligand. The presence of this ammonium salt was identified by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and its presence made purification by column chromatography very difficult, but attempts to remove the proton by DBU were successful. The neutral complexes (**6**) and (**7**) were isolated, after deprotonation, by precipitation from a CH_2Cl_2–hexane solution followed by extraction with ether.

Following the reaction with DBU, the $\nu(C{\equiv}C)$ stretching frequency changed from 2084 to $2070\,cm^{-1}$ for **6**, but after reaction of the osmium analogue (**7**) with DBU, the $\nu(C{\equiv}C)$ stretching frequency increased to $2088\,cm^{-1}$. **6** could be recrystallised by a two-layered CH_2Cl_2 – hexane system yielding dark orange crystals, which gave good NMR spectra and microanalysis but were unsuitable for X-ray structural analysis. Attempts to purify the osmium analogues led to decomposition of the complexes and made interpretation of the NMR data difficult.

The attempted synthesis of the chiral ferrocenyl analogue of $[(\eta\text{-}C_5H_5)(Ph_3P)_2RuC{\equiv}C(C_5H_4)Fe(C_5H_5)]$, previously reported by Sato et al. [16], supported the suggestion that the chiral ethynylferrocene was acting as a base. This reaction should proceed through a vinylidene intermediate which is converted to the acetylide product by addition of a base (sodium methoxide solution). However, once again the ammonium salt-acetylide {$\nu(C{\equiv}C)$ $2070\,cm^{-1}$} was formed before the addition of a base. Attempts to convert the charged species to the neutral complex by reaction with DBU in CH_2Cl_2 were unsuccessful.

2.2. Electrochemistry

The electrochemical behaviour of (**4**, **5**, **6a**, **7a**, **6**, **7**) was analysed by cyclic voltammetry in order to elucidate whether the chiral complexes showed the same electrochemical properties as their non-chiral analogues [13,14,17] (Scheme 4). The experiments were recorded at 298 K on a standard three-electrode system (platinum



Scheme 4. Analogous non-chiral ferrocenyl-metal complexes.

Table 1
Electrode potentials and related data

Complex	$E_{1/2/\mathrm{I\,std}}$ (V)	$\Delta E_{p/\mathrm{I}}$ (V)	$E_{1/2/\mathrm{II\,std}}$ (V)	$\Delta E_{p/\mathrm{II}}$ (V)	$\Delta E_{1/2}$ (V)
8	0.12	0.07			
4	0.40	0.10			
9	−0.08	0.09	0.84 *		0.94
10	−0.38	0.14	0.32	0.15	0.70
11	−0.44	0.08	0.21	0.08	0.65
6a	0.10	0.10	0.57	0.10	0.47
7a	0.05	0.10	0.53	0.10	0.48

Scan rate 100 mV s^{-1}. All $E_{1/2}$ referenced to $FeCp_2$ in the same system. $E_{1/2/\mathrm{I\,std}}$ iron electrode potential, $E_{1/2/\mathrm{II\,std}}$ manganese, osmium or ruthenium electrode potential. * Irreversible wave E_{pA} quoted only.

working/auxiliary electrodes and silver wire reference electrode) using 0.1 M $[NBu^n_4][BF_4]/CH_2Cl_2$ as supporting electrolyte. All $E_{1/2}$ values were referenced using an internal ferrocene reference ($E_{1/2}$ $FeCp_2$ = 0.0 V) and are reported in Table 1.

The chiral ethynylferrocene ligand (**4**) has a quasi-reversible $Fe^{II/III}$ redox couple ($\Delta E_p = 0.10$ V), with an electrode potential of 0.4 V, this value being 0.28 V more anodic than that of the non-chiral analogue (**8**). The data in Table 1 show clearly that the substitution of the original ethynylferrocene ligand in complexes (**9–11**) with **4**, alters the electrochemical properties of these systems.

The electrode potentials of the metal centres in **6a** and **7a** are more anodic than those in the non-chiral analogues (Fig. 1). The cyclic voltammograms of complexes **5**, **6** and **7** did not yield clear results due to the instability of these complexes in the electrolyte, but the graphs did suggest that, in each case, the $Fe^{II/III}$ redox couple was more anodic than the standard ferrocene. These findings were supported by the fact that **5**, **6** and **7** could not be chemically oxidised to the mixed-valence systems ($[Fe^{III}M^{II}][PF_6]$) by reaction with $[Fc][PF_6]$. Any attempts to synthesise the mixed-valence systems of the complexes therefore require a stronger chemical oxidant.

Overall, the electrochemical experiments indicate that the difference between the electrode potentials of the two metal centres in the chiral heterobimetallic system is less than that in the non-chiral analogue. Therefore, there will be a decrease in the degree of polarisation in the chiral systems compared with the non-chiral complexes. This suggests that there will be a decrease in metal-to-metal interaction, as neither metal will have sufficient excess of electronic charge to donate to the other. The metal-to-metal interaction could not be measured as it was not possible to synthesise the mixed-valence chiral systems.

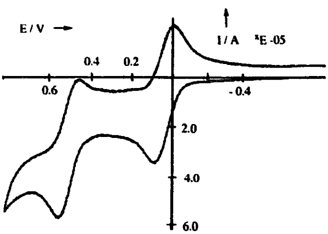


Fig. 1. Cyclic voltammogram of the protonated chiral ferrocenyl-osmium complex (**7a**).

2.3. SHG measurements

The second-order NLO activity of the chiral complexes depends on whether or not the chiral ferrocenyl ligand can induce correct non-centrosymmetric packing in the complexes (**5–7**). However, since none of the chiral complexes gave crystals suitable for X-ray structure analysis, the crystal packing could not be identified. The chiral complexes were nevertheless subjected to testing by Kurtz powder techniques in order to establish the degree of NLO behaviour.

The complexes did not exhibit any detectable signals with regard to second-order NLO activity. It was assumed that these poor SHG results were due to crystallisation in a pseudo-centrosymmetric space group (probably $P2_12_12_1$), and possibly low β values for the chromophores. Previous reports [18] have explained negligible SHG results through an unfavourable alignment of the chromophores in the crystal lattice of other ferrocene-type species. Despite fulfilling the known criteria for second-order NLO activity, the complexes exhibit negligible NLO activity. Clearly, a new approach is required to improve synthetic routes and crystallographic design. The synthesis of other chiral ferrocenyl centres is proposed, as the smallest change in the ferrocenyl substituents might help induce greater non-centrosymmetric character, which in turn should have a major effect on NLO activity of the system. Further crystallographic and optical studies are also needed if the optical non-linearities of organometallic compounds are to be fully understood and exploited.

3. Experimental

3.1. General

All preparations were carried out using standard Schlenk techniques [19]. All solvents were distilled over standard drying agents under nitrogen directly before use and all reactions were carried out under an atmosphere of nitrogen.

Alumina gel (type UG-1) and silica gel (230–400 mesh) were used for chromatographic separations.

All NMR spectra were recorded on Bruker instruments, operating at either 250 or 400 MHz. Chemical shifts are reported in δ using $CDCl_3$ (^1H δ 7.25 ppm, ^{13}C δ 77.0 ppm) as the reference for ^1H and $^{13}C\{^1H\}$ spectra, while the $^{31}P\{^1H\}$ spectra were referenced to trimethylphosphite. Infrared spectra were recorded using NaCl solution cells (CH_2Cl_2) with a Perkin-Elmer 1710 Fourier Transform IR spectrometer. Mass spectra were recorded using positive FAB methods, on a Kratos MS60 spectrometer. Microanalyses were carried out at the Department of Chemistry, University of Cambridge. The electrochemistry was recorded using an Autolab PGSTAT 20 potentiostat with a standard three-electrode system (platinum working/auxiliary electrodes and silver wire reference electrode). The electrochemical experiments were measured at 298 K using a 0.1 M $[NBu^n_4][BF_4]/CH_2Cl_2$ (solvent dried over CaH_2) solution as supporting electrolyte, and all solutions were purged with N_2. All electrochemical measurements were referenced using an internal ferrocene reference ($E_{1/2}$ $FeCp_2$ = 0.0 V at 298 K in 0.1 M $[NBu^n_4][BF_4]/CH_2Cl_2$). Powder second harmonic generation studies were undertaken using 8 ns pulses of light at a wavelength of 1.064 μm from a Q-switched Nd-YAG laser. A powdered sample of urea was used as a reference standard. The experimental limit of detection in reflection from the samples was determined to be approximately 1% of the signal at 532 nm obtained from the urea.

3.2. Synthesis of chiral ferrocene ligands

N,N-dimethylaminoethylferrocene (**1**) was synthesised from carboxylferrocene and resolved into its optically pure isomers $\{[\alpha]^{25}_D \pm 14.0$ (c 1.6, ethanol)$\}$ using literature procedures [7,9] in yields comparable with those reported.

3.2.1. [N,N-dimethylaminoethyliodoferrocene] (2)

(2.0 g, 7.84 mmol) of either the R or S isomer of **1** was dissolved in 25 cm^3 of diethyl ether. 1.6 M *n*-BuLi in hexane (5 cm^3, 8.0 mmol) was added at room temperature. The solution was stirred for 1 h and then cooled to −78 °C, after which a solution of iodine (2.0 g, 7.94 mmol, in 100 cm^3 of diethylether) was added under vacuum via a cannular. The mixture was stirred for a further 1 h at −78 °C and then brought to room temperature. After addition of water (25 cm^3) the solution was stirred for a further 0.5 h, when it was extracted several times with ether. The organic layer was dried over $CaCl_2$ for 24 h in the dark with stirring. The solvent was removed and the residual oil was purified on a column using diethylether as eluent. The first and major fraction contained N,N-dimethylaminoethyliodoferrocene as a dark orange oil (1.5 g, 50%). No optical measurements were taken of **2** because the isolated product was a mixture of diastereoisomers which could not be separated on an alumina column. [(**1**)(R)-] → {[(**2**)(R)-(R)] 4%, [(**2**)(R)-(S)] 96%}.

Anal. Found: C, 44.4; H, 4.82; N, 3.59. $C_{14}H_{18}NIFe$ Calc.: C, 44.0; H, 4.7; N, 3.67%. δ_H ($CDCl_3$): 1.52 (3H, d), 2.13 (6H, s), 3.61 (H, q), 4.13 (5H, s), 4.14 (H, q), 4.23 (H, q), 4.45 (H, q). δ_C ($CDCl_3$): 16.0 ($C^{\$}$), 41.2 ($C^{£}$), 45.4 ($C_1$), 57.6 ($C^{!}$), 65.6 ($C_2$), 68.2 ($C_3$), 71.7 ($C_4$), 74.3 ($C_5$), 90.1 ($C_6$) {$C^{\$}$ = single methyl, $C^{£}$ = amine methyls, $C^{!}$ = chiral carbon, C_1 to C_6 = ferrocenyl carbons}. m/z 383 (M^+).

3.2.2. [N,N-dimethylaminoethyltrimethylsilylethynylferrocene] (3)

Compound (**2**) (1.0 g, 2.6 mmol) was dissolved in 100 cm^3 of diisopropylamine. This solution was then cooled to 0 °C and TMSA (0.6 g, 6.1 mmol) was added. Catalytic amounts of CuI (30 mg), $Pd^{II}(OOCCH_3)_2$ (30 mg) and PPh_3 (90 mg) were added simultaneously and the mixture was stirred at 0 °C for 0.5 h. The solution was then warmed to room temperature and stirred for another 0.5 h. The reaction mixture was refluxed for 24 h in the absence of light and a white precipitate formed overnight, indicating that the reaction had taken place. The reaction mixture was cooled to room temperature and diethylether (100 cm^3) was added. The solution was filtered and the solvent removed yielding an orange oil. This crude product was purified using two successive alumina columns with diethylether as eluent. The major fraction was an orange band which, upon removal of solvent, gave an orange crystalline powder N,N-dimethylaminoethyltrimethylsilylethynyl ferrocene (**3**) (1.0 g, 70%). Note: the starting material (**2**) was a diastereoisomeric mixture (96:4), and both isomers react to give the same ratio of ethynyl products. These diastereoisomers were separated on the column, the lower percentage diastereoisomer was red in colour and was eluted before the major product which was an orange band.

Anal. Found: C, 64.0; H, 7.7; N, 3.72. $C_{19}H_{27}NFeSi$ Calc.: C, 64.6; H, 7.65; N, 3.97%. Optical activity $[\alpha]^{25}_D + 77.51/-75.2$ (c 0.2, $CHCl_3$). $\nu(C{\equiv}C)$ (cm^{-1}): 2148 (CH_2Cl_2). δ_H ($CDCl_3$): 0.19 (9H, s), 1.54 (3H, d), 2.12 (6H, s), 3.74 (H, q), 4.12 (5H, s), 4.14 (H, m), 4.15 (H, t), 4.40 (H, t). δ_C ($CDCl_3$): 0.53 ($C^{@}$), 18.3

($C^{\$}$), 41.2 ($C^{\pounds}$), 56.2 ($C^{!}$), 65.6 ($C_1$), 65.9 ($C_2$), 67.3 ($C_3$), 67.4 ($C_4$), 70.6 ($C_5$), 90.0 ($C_6$), 93.0, 104.2 ($C^{*}$) {$C^{@}$ = TMS carbons, $C^{\$}$ = single methyl, $C^{\pounds}$ = amine methyls, $C^{!}$ = chiral carbon, C_1 to C_6 = ferrocenyl carbons, C^{*} = acetylide carbons}. *m/z* 353 (M^+).

3.2.3. *[N,N-dimethylaminoethylethynylferrocene] (4)*

Complex (**3**) (1.0 g, 2.8 mmol) was dissolved in methanol (50 cm^3) and diethylether (10 cm^3) and powdered anhydrous K_2CO_3 (0.5 g) was added to the solution. The reaction mixture was left stirring overnight and shielded from light. The resultant IR spectrum indicated that the reaction was complete. The solvent was removed and the solid was dissolved in diethylether and washed with water. The organic layer was dried over $MgSO_4$ overnight with stirring in the dark. The solution was filtered and reduced to an oil under vacuum. On standing, this oily residue formed an orange crystalline solid, N,N-dimethylaminoethylethynylferrocene (**4**) (0.7 g, 88%).

Anal. Found: C, 68.18, H, 6.89, N, 4.91. $C_{16}H_{19}NFe$ Calc.: C, 68.4; H, 6.76; N, 4.98%. Optical activity $[\alpha]_D^{25}$ + 45.0/ − 40.2 (c 0.2, $CHCl_3$). $\nu(C\equiv C)$ (cm^{-1}): 2108; ν(C–H) 3305 (CH_2Cl_2). δ_H ($CDCl_3$): 1.56 (3H, d), 2.01 (6H, s), 2.83 (H, s), 3.82 (H, q), 4.13 (5H, s), 4.16 (H, m), 4.19 (H, t), 4.46 (H, t). δ_C ($CDCl_3$): 17.8 ($C^{\$}$), 41.1 ($C^{\pounds}$), 56.2 ($C^{!}$), 64.6 ($C_1$), 67.3 ($C_2$), 70.7 ($C_3$), 71.0 ($C_4$), 71.6 ($C_5$), 90.3 ($C_6$), 75.8, 82.4 ($C^{*}$) ppm {$C^{\$}$ = single methyl, $C^{\pounds}$ = amine methyls, $C^{!}$ = chiral carbon, C_1 to C_6 = ferrocenyl carbons, C^{*} = acetylide carbons}. *m/z* 281 (M^+).

3.3. *Synthesis of chiral ferrocenyl metal-acetylides*

The metal halides [*cis*-Ru(dppm)$_2$Cl$_2$] [20,21], [*cis*-Os(dppm)$_2$Cl$_2$] [20] and [*fac*-Mn(CO)$_3$(dppm)Br] [22] were all synthesised using published procedures.

3.3.1. *Fac-[(dppm)(OC)$_3$MnC$\equiv$CC$_5$H$_3$(CHMe(NMe$_2$))Fe(C$_5$H$_5$)] (5)*

Complex (**4**) (0.1 g, 0.35 mmol) was dissolved in THF (20 cm^3) and *n*-BuLi (2.5 cm^3, 1.6 M, 0.4 mmol) was added at room temperature. This mixture was left stirring for 1 h, after which *fac*-[Mn(dppm)(CO)$_3$Br] (0.22 g, 0.35 mmol) was added and the mixture was stirred for 24 h. The organic layer was then washed several times with water and finally dried over anhydrous $MgSO_4$. The solvent was removed and the resultant orange solid was dissolved in CH_2Cl_2 and applied to an alumina column. The reaction products were eluted using ethyl acetate as eluent. The second orange band was [(dppm)(OC)$_3$MnC$\equiv$CC$_5$H$_3$(CHMe(NMe$_2$))-Fe(C$_5$H$_5$)], which was recrystallised from a CH_2Cl_2/hexane two-layered system to yield orange needles (**5**) (0.025 g, 25%).

Anal. Found: C, 66.4; H, 5.6; N, 1.4. $C_{44}H_{40}P_2NO_3FeMn$ Calc.: C, 65.8; H, 5.0; N, 1.7%. $\nu(C\equiv C)$ (cm^{-1}): 2094; ν(CO) 2012, 1940, 1919 (CH_2Cl_2). δ_H ($CDCl_3$): 1.58 (3H, d, Me of chiral centre), 2.11 (6H, s, Me$_2$ on amine), 3.70 (H, q, proton on chiral centre), 4.24 (7H, m, ferrocenyl protons), 4.51 (H, s, Cp–H), 4.65 (4H, m, dppm protons), 6.5–8.0 (40H, m, dppm aromatic protons), 8.25 (H, bs, ammonium proton). δ_C insufficient sample. δ_P (CD_2Cl_2): − 119. *m/z* 804 (M^+).

3.3.2. *Trans-[Cl(dppm)$_2$RuC$\equiv$CC$_5$H$_3$(CHMe(NH-Me$_2$))Fe(C$_5$H$_5$)][PF$_6$] (6a)*

N,N-dimethylaminoethylethynylferrocene (**4**) (0.050 g, 0.18 mmol) was added to a solution of *cis*-[Ru(dppm)$_2$Cl$_2$] (0.17 g, 0.18 mmol) and $NaPF_6$ (0.060 g, 0.36 mmol) in CH_2Cl_2 (30 cm^3). This mixture was stirred for 4 h, during which time the solution became dark orange. The reaction was monitored by IR spectroscopy. The disappearance of the ν(C–H) stretching frequency indicated completion of the reaction. The solution was then filtered and the solvent was removed, yielding [Cl(dppm)$_2$RuC$\equiv$CC$_5$H$_3$(CHMe(NHMe$_2$))-Fe(C$_5$H$_5$)][PF$_6$] (**6a**) as an orange solid (0.2 g, 83.4%).

Anal. Found: C, 58.9; H, 4.7; N, 1.0. [$C_{66}H_{63}P_4NClFeRu$][PF$_6$] Calc.: C, 59.6; H, 4.7; N, 1.1%. $\nu(C\equiv C)$ (cm^{-1}): 2085 (CH_2Cl_2). δ_H ($CDCl_3$): 1.35 (3H, d, Me of chiral centre), 1.89, 1.99, 2.12, 2.33 (6H, d, Me$_2$ on ammonium salt), 3.65 (H, d, proton on chiral centre), 4.0–4.2 (8H, m, ferrocenyl protons), 4.65 (4H, m, dppm protons), 6.5–8.0 (40H, m, dppm aromatic protons), 8.25 (H, bs, ammonium proton). δ_C ($CDCl_3$): 15.2 ($C^{\$}$), 40.8, 41.6 ($C^{\pounds}$), 46.0 ($C^{!}$), 62.1 ($C_1$), 65.8 ($C_2$), 70.0 ($C_3$), 70.1 ($C_4$), 70.3 ($C_5$), 125–135 ($C^{@}$) {$C^{\$}$ = methyl on chiral carbon, $C^{\pounds}$ = methyls on ammonium salt, $C^{!}$ = CH_2 of dppm, C_1 to C_5 = ferrocenyl carbons, $C^{@}$ = dppm aromatic carbons, acetylide carbons were too weak to assign. δ_P (CD_2Cl_2): − 140, − 170, complicated multiplets. *m/z* 1186 (M^+).

3.3.3. *Trans-[Cl(dppm)$_2$OsC$\equiv$CC$_5$H$_3$(CHMe(NH-Me$_2$))Fe(C$_5$H$_5$)][PF$_6$] (7a)*

The synthesis of **7a** was carried out as for **6a** using compound (**4**) (0.05 g, 0.18 mmol), *cis*-[Os(dppm)$_2$Cl$_2$] (0.18 g, 0.18 mmol) and $NaPF_6$ (0.06 g, 0.36 mmol). Subsequent purification by recrystallisation from a CH_2Cl_2/hexane two-layered system yielded very small amounts of an orange solid [Cl(dppm)$_2$OsC$\equiv$CC$_5$H$_3$-(CHMe(NHMe$_2$))Fe(C$_5$H$_5$)] [PF$_6$] (**7a**).

Anal. Found: C, 54.9; H, 4.64; N, 1.49. [$C_{66}H_{63}P_4NClFeOs$][PF$_6$] Calc.: C, 55.8; H, 4.4; N, 0.98%. $\nu(C\equiv C)$ (cm^{-1}): 2084 (CH_2Cl_2). δ_H ($CDCl_3$): 1.44 (3H, d, Me of chiral centre), 1.96 (d), 2.15 (t), 2.37 (d) (6H, Me$_2$ on ammonium salt), 3.72 (H, d, proton on chiral centre), 4.0–4.3 (8H, m, ferrocenyl protons), 4.71 (4H, m, dppm protons), 6.5–8.0 (40H, m, dppm aromatic protons), 8.42 (broad, H, ammonium proton). δ_C

insufficient sample. δ_P (CD_2Cl_2): −180, −210 complicated multiplets. m/z 1276.0 (M^+).

3.3.4. *Trans-[Cl(dppm)$_2$RuC≡CC$_5$H$_3$(CHMe(NHMe$_2$))Fe(C$_5$H$_5$)] (6)*

Complex (**6a**) (0.2 g, 0.15 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and DBU (0.025 g, 0.15 mmol) added to the stirred solution. After 2 h stirring, the solution was filtered and the solvent was removed in vacuo. The residual orange solid was dissolved in CH_2Cl_2/hexane solution. The CH_2Cl_2 was evaporated slowly at room temperature under vacuum. The brown oil which deposited on the flask was discarded and the yellow solution was reduced to a fine yellow solid which was repeatedly extracted with diethylether. The ether was removed in vacuo and the solid washed with hexane. The resultant solid [Cl(dppm)$_2$RuC≡CC$_5$H$_3$(CHMe(NHMe$_2$))Fe(C$_5$H$_5$)] (**6**) was recrystallised from a CH_2Cl_2/hexane two-layer system, yielding orange crystals (0.1 g, 56%).

Anal. Found: C, 66.6; H, 5.7; N, 1.4. $C_{66}H_{62}P_4NCFeRu$ Calc.: C, 66.9; H, 5.2; N, 1.2%. ν(C≡C)(cm^{-1}): 2070 (CH_2Cl_2). δ_H ($CDCl_3$): 0.98 (3H, d, Me of chiral centre), 1.97 (6H, Me$_2$ of amine), 2.65 (H, q, proton on chiral centre), 3.51 (SR, s, Cp), 3.61 (H, t, Cp–H), 3.74 (2H, d, Cp–H), 5.01 (4H, m, dppm protons), 7.0–7.7 (40H, m, dppm aromatic protons). δ_C ($CDCl_3$): 10.3 ($C^{\$}$), 40.5 ($C^{\pounds}$), 49.5 ($C^{!}$), 55.2 ($C^{\&}$), 64.1 ($C_1$), 65.2 ($C_2$), 69.2 ($C_3$), 69.6 ($C_4$), 88.7 ($C_5$), 105 ($C^{*}$), 125–137 ($C^{@}$) {$C^{\$}$ = methyl on chiral carbon, $C^{\pounds}$ = methyls on amine, $C^{!}$ = CH$_2$ of dppm, $C^{\&}$ = chiral carbon, C_1 to C_5 = ferrocenyl carbons, C^{*} = acetylide carbons, $C^{@}$ = dppm aromatic carbons}. δ_P (CD_2Cl_2): −143 (t), −146 (t), −148 (s). m/z 1187 (M^+).

3.3.5. *Trans-[Cl(dppm)$_2$OsC ≡ CC$_5$H$_3$(CHMe(NHMe$_2$))Fe(C$_5$H$_5$)] (7)*

Complex (**7a**) (0.2 g, 0.14 mmol) was dissolved in CH_2Cl_2 (20 cm^3), followed by addition of DBU (0.025 g, 0.15 mmol) and the solution stirred for 2 h. The reaction product [Cl(dppm)$_2$OsC≡CC$_5$H$_3$(CHMe(NHMe$_2$))Fe(C$_5$H$_5$)] (**7**) was worked-up as for **6**. Recrystallisation of **7** led to decomposition of the complex. Therefore ^{1}H, ^{13}C and ^{31}P NMR data could not be interpreted and the analysis was incorrect due to impurities. ν(C≡C) (cm^{-1}): 2088 (CH_2Cl_2). m/z 1276.0 (M^+).

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