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The synthesis and X-ray crystal structure of [(4-ferrocenylphenylimido)]trichlorobis(triphenylphosphine)rhenium(V) and related ferrocenyl–rhenium(V) compounds†

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The reaction of 4-ferrocenylaniline with *trans*-[ReOCl$_3$(PPh$_3$)$_2$] gave [(4-ferrocenylphenylimido)]trichlorobis(triphenylphosphine)rhenium(V) (**1**). The molecular structure of **1** has been determined by X-ray diffraction. The X-ray crystal structure of [(4-ferrocenylphenylimido)]tribromobis(triphenylphosphine)rhenium(V) (**2**) has also been determined and its molecular structure is compared with that of **1**. The complexes **1** and **2** have also been investigated by cyclic voltammetry and UV-visible spectroscopy. The results of the cyclic voltammetry suggest that there is insignificant electron delocalization from the ferrocenyl group towards rhenium in **1** and **2**. However, both **1** and **2** show a long wavelength absorption in their electronic spectra which is characteristic of conjugated ferrocenyl derivatives. The synthesis and characterization of two further similar imido-complexes but in which the ferrocenyl-phenyl group is part of a more extended unit is described (complexes **5** and **6**). The synthesis of a rhenium oxo-complex, *fac*-oxotrichloro[1,1′-bis(diphenylphosphine)ferrocene]rhenium(V) (**3**) has also been achieved and **3** has been further derivatized with two different ferrocenylamines to provide rhenium complexes containing two ferrocenyl groups (**4** and **7**).

Introduction

The current interest in organometallic compounds in the field of new materials for applications in 21st century technology is significant and developments in ferrocene and metallocene chemistry are leading the way in this respect.[1] We are interested in the design of ferrocenomesogens with new interesting shapes and structures, especially ones in which the ferrocenyl group is at the terminal position in a molecule.[2] The molecules in the first series of ferrocenomesogens reported by us incorporated a terminal ferrocenyl group onto a rod-like organic core and the compounds are represented by the general structure shown in Fig. 1.[2] Recently we have become interested in the effect of introducing a second metal into such a molecule, in which the second metal is in conjugation with the ferrocenyl group. Here, we report on the synthesis and X-ray crystal structure determination of [(4-ferrocenylphenylimido)]trichlorobis(triphenylphosphine)rhenium(V) (**1**) which is one of the first examples of an imido-rhenium(V) complex with an appended organometallic group. We also report on the X-ray crystal structure of [(4-ferrocenylphenylimido)]tribromobis(triphenylphosphine)rhenium(V) (**2**) and on the synthesis and structure of a ferrocenyl–rhenium oxo-compound, *fac*-oxotrichloro(1,1′-bis(diphenylphosphine)ferrocene)]rhenium(V) (**3**). Furthermore, we report on the reaction of two different ferrocenylamines with **3** to provide ferrocenyl–rhenium complexes containing two ferrocenyl groups (compounds **4** and **7**). Finally, the syntheses of a further two compounds similar to **1** but in which the ferrocenyl ligand is part of a more extended structure are reported (compounds **5** and **6**).

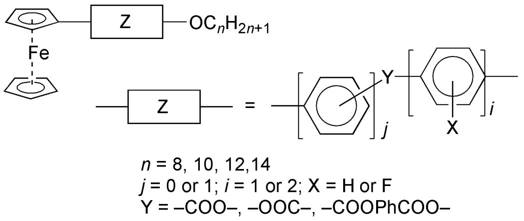

Fig. 1 General structure representing the first series of ferrocenomesogens prepared by Imrie and Loubser.

A number of reports have been published on the synthesis and structure of arylimido-complexes of rhenium(V).[3] The majority of these studies are concerned with the chemistry of [(phenylimido)]trichlorobis(triphenylphosphine)rhenium(V), and the others with compounds containing simple substituents at the *para* position in the phenyl group. Interest in these compounds stems from their potential use either as metathesis catalysts or therapeutic radiopharmaceuticals. There are a number of examples of rhenium complexes with ferrocenyl ligands in the literature[4] but most involve low oxidation state Re(I) carbonyl compounds with ferrocenylphosphine ligands. For example, the structures of the compounds [Fe(C$_5$H$_4$PPh$_2$)$_2$-Re(CO)$_3$Cl] (**8**) and *fac*-[(FeC$_5$H$_4$PPh$_2$)$_2$Re(CO)$_3$Cl] (**9**) have

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† Electronic supplementary information (ESI) available: spectroscopic details for starting materials; Re=O bond distances in compounds of the type ReOCl$_3$(PR$_3$)$_2$. See http://www.rsc.org/suppdata/dt/b1/b102372c/

‡ Part of this work was carried out by Dr Imrie during his visit to the ICL, Oxford.

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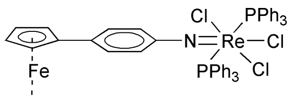

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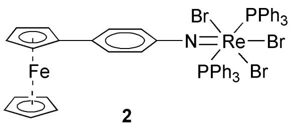

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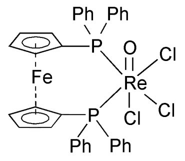

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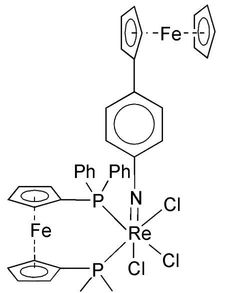

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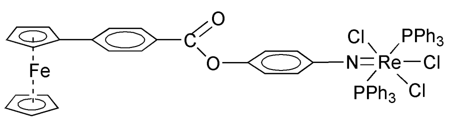

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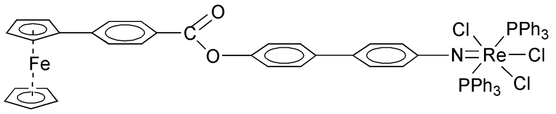

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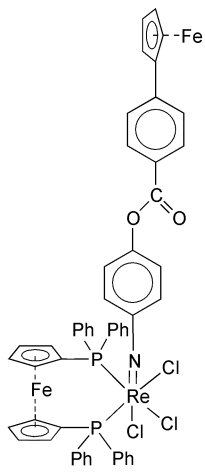

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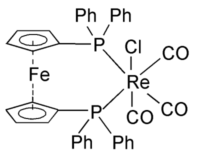

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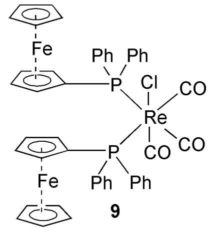

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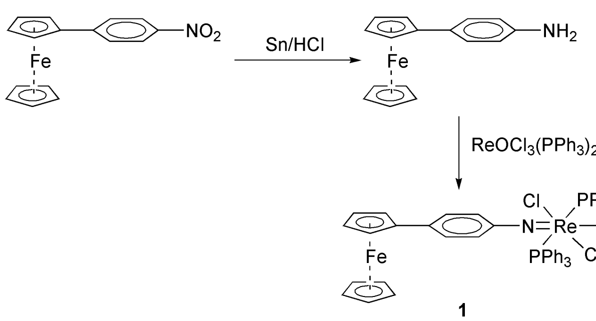
been determined by X-ray crystallography.[4a] An exception is the Re(v) complex [ReO(L)(PPh$_3$)][PF$_6$] (H$_2$L = 1,6-diferrocenyl-*N*,*N′*-bis(2-hydroxypropyl)-2,5-diazahexane.[4e]

Recently, Knoesen *et al.*[5] have published work on ferrocenyl ligands in mixed valence high-oxidation state rhenium complexes. As part of their paper, the synthesis and X-ray crystal structure determination of compound **3** is also described. The crystal structure of the phenylimido derivative of compound **3** has been described recently by Lee and Choi.[6]

Results and discussion

Preparation of [(4-ferrocenylphenylimido)]trichlorobis(triphenylphosphine)rhenium(v)

[(4-Ferrocenylphenylimido)]trichlorobis(triphenylphosphine)-rhenium(v) **1** was synthesized by reacting 1.5 equivalents of 4-ferrocenylaniline with *trans*-oxotrichlorobis(triphenylphosphine)rhenium(v) in benzene (Scheme 1). Compound **1** was readily purified by passing it through a column of silica gel. The compound eluted with diethyl ether as a red band but on removing the solvent, a blue-green solid was obtained. The blue-green solid exhibited a low solubility in diethyl ether but was readily soluble in dichloromethane. The blue-red colour interchange was observed when running **1** on a tlc plate. On elution of the initial dark-blue/green spot with diethyl ether, it rapidly turned red and returned to green again after evaporation of the diethyl ether. Compound **1** was characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy as well as by IR and FAB mass spectrometry. The NMR data for **1** are consistent with its structure and are discussed more fully below. The IR spectrum contains a band at 1092 cm^{-1} which falls in the range for a Re=N bond.



Scheme 1 Preparation of complex **1**.

X-Ray crystal structure of *trans*-[(4-ferrocenylphenylimido)]-trichlorobis(triphenylphosphine)rhenium(v) (1)

Suitable crystals of **1**·CH$_2$Cl$_2$ were grown by slow evaporation of a solution in dichloromethane–hexane. The ZORTEP structure of **1** is shown in Fig. 2 and the packing diagram is shown in Fig. 3. A selection of bond lengths and angles are provided in Table 1. The coordination geometry around the rhenium atom is distorted octahedral. The chloride ligands are in a meridional-configuration and the triphenylphosphine ligands are *trans*. The ligand arrangement around the rhenium is consistent with the spectroscopic data for **1** in solution. The Re–N bond length in **1** is 1.724(18) Å. It is interesting to compare this value with the Re–N bond lengths for similar compounds in which the ferrocenyl unit is replaced by other substituents (Table 2). The range of substituents at the *para* position is rather limited but they cover the spectrum from electron-releasing groups through to an electron-withdrawing group. The variation in Re–N bond length with substituent shows little clear evidence for any imido substituent effect. Chatt *et al.*[7] investigated the dipole moments of a series of arylimido-complexes of rhenium and developed an argument that an electron-releasing group *para* to the nitrogen in this type of system can be expected to cause a drift of electrons towards the nitrogen, and this in turn should lead to an enhanced interaction of the nitrogen lone pair electrons with the d-orbitals of the rhenium atom. This should however be reflected in the Re–N bond length with an expectation that as the substituent becomes a more efficient electron-donor, the rhenium–nitrogen bond should take on a greater triple bond character and so should become considerably shorter.

The extent to which electron density is removed from the ferrocenyl group manifests itself as a distinct trend in the

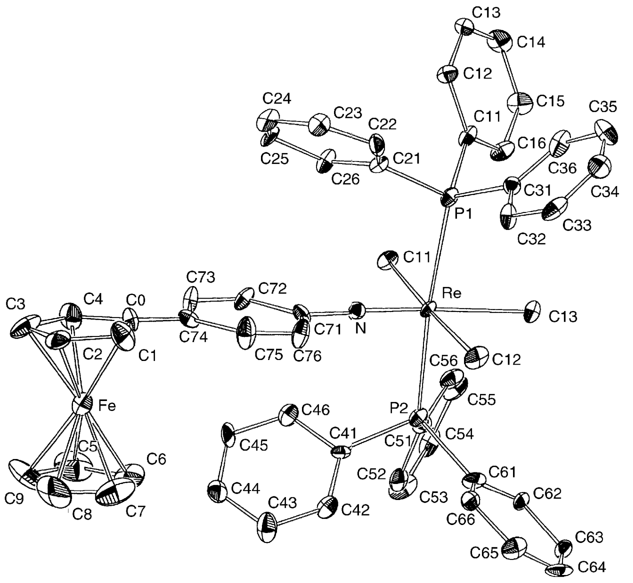


Fig. 2 Molecular structure of **1** with numbering scheme.

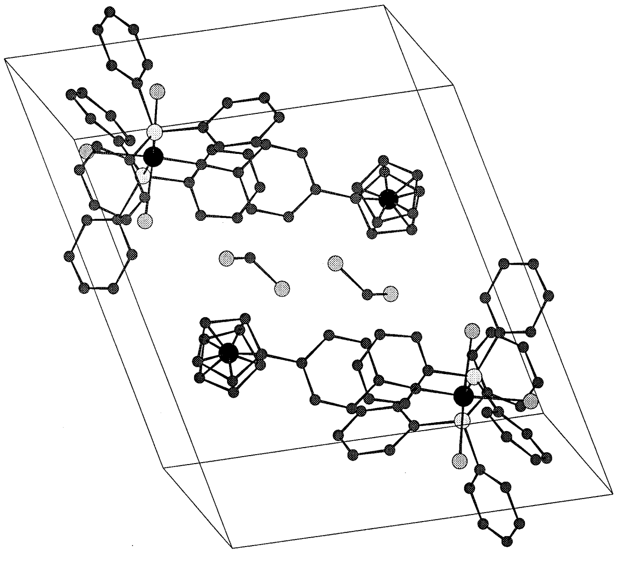


Fig. 3 Packing diagram for compound **1**.

^{1}H chemical shifts of the C_5H_4 protons. Selected values of the chemical shifts obtained from some ferrocenylphenyl-derivatives prepared by us (**10**) in other work[2c] are given in Fig. 4 together with ferrocenylphenyl-derivatives prepared by other workers (**11** and **12**) and help to illustrate this point, and make an interesting comparison with compound **1**. Compounds having the general structures **10**, **11** and **12** have a number of common features. Firstly, each contains a ferrocenylphenyl group to which is attached an electron-withdrawing group. Secondly, the chemical shift values of the Cp protons for these molecules are remarkably similar (α-Hs all in the range 4.69–4.77). Compounds **11** and **12** exhibit significant non-linear optical activity arising from the asymmetric charge distribution along the molecular framework, electrons flowing from the ferrocenyl group towards the 4-nitrophenyl group.[8] If the electron-withdrawing substituents on compounds **11** and **12** are replaced with groups such as amino and methoxy which donate electrons into the aromatic ring, the chemical shifts for the α-Hs on the Cp ring fall to 4.54 ppm and 4.58 ppm respectively. In comparison, the chemical shift value of the α-Hs in **1** (4.61 ppm) is similar to the situation where we have an electron-

Table 1 Selected bond lengths (Å) and bond angles (°) for compounds **1** and **2**

Compound **1**		Compound **2**	
Re–N	1.724(18)	Re–N	1.721(4)
Re–Cl1	2.413(5)	Re–Br1	2.5561(5)
Re–Cl2	2.434(5)	Re–Br2	2.5884(5)
Re–Cl3	2.397(6)	Re–Br3	2.5649(5)
Re–P1	2.497(6)	Re–P1	2.4963(13)
Re–P2	2.483(7)	Re–P2	2.4925(13)
N–C71	1.350(3)	N–C71	1.351(3)
P1–C31	1.820(2)	P1–C31	1.839(5)
C71–C72	1.420(3)	C71–C72	1.386(7)
C72–C73	1.340(3)	C72–C73	1.376(7)
C73–C74	1.390(3)	C73–C74	1.383(8)
CO–C74	1.450(3)	CO–C74	1.459(7)
N–Re–Cl3	175.1(5)	N–Re–Br3	173.95(13)
N–Re–Cl1	93.5(5)	N–Re–Br1	93.50(13)
Cl3–Re–Cl2	84.7(2)	Br3–Re–Br2	85.059(18)
Cl1–Re–Cl2	176.0(2)	Br1–Re–Br2	177.601(18)
N–Re–P (2)	95.5(6)	N–Re–P2	95.16(13)

Table 2 Re–N bond distances (Å) in compounds of the type $[ReCl_3(NC_6H_4X)(PR_3)_2]$

R	X	Re–N	Ref.
Ph	Ferrocenyl	1.724(18)	This work
Et_2Ph	OCH_3	1.709(4)	3*a*
Ph	H	1.726(6)	3*b*
CH_3	H	1.711(6)	3*c*
Ph	$CH_2CH_2CH_2CO_2CH_2CH_3$	1.713(4)	3*d*
Et_2Ph	$COCH_3$	1.690(5)	3*a*
OCH_3	H	1.710(8)	3*c*

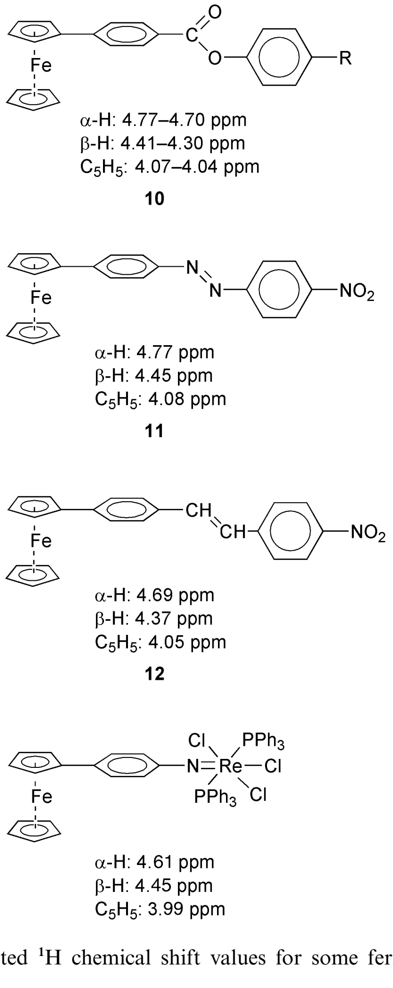


Fig. 4 Selected ^{1}H chemical shift values for some ferrocenylphenyl derivatives.

donating group attached to the ferrocenylphenyl unit. The NMR results provide no evidence therefore for significant electron flow from the ferrocenyl unit towards the rhenium metal. If delocalization in the sense Fe ⟶ Re was significant this should also be reflected in the X-ray crystal structure in that the phenyl ring next to the ferrocenyl group would tend towards a cyclohexadienyl structure which should lead to a reasonable reduction in bond length between C73–C72 and C75–C76. There are however no significant bond length differences in the linking phenyl group.

The ferrocenylphenyl imido group has a linear Re–N–C system indicative of formal donation of four electrons from the imido group. The angles N–Re–Cl3 (175.1°) and Cl1–Re–Cl2 (176.0°) deviate only marginally from the ideal linear arrangement. The Re–Cl bond distances in positions *trans* and *cis* to the imido ligand do not show significant differences. The Re–Cl bond (mean 2.415 Å) and the Re–P bond distances in **1** (mean 2.490 Å) are also closely similar to those of related compounds.[3]

The packing diagram of **1** (Fig. 3) clearly shows the presence of dichloromethane in the crystal lattice and the NMR results confirm its presence. The closest atomic distance between the carbon atom of the solvent (C14) and **1** is to C66, but this is 3.73 Å. The solvent resides in cavities in the crystal lattice.

Preparation of *trans*-[(4-ferrocenylphenylimido)]tribromobis(triphenylphosphine)rhenium(V) (2)

Compound **2** was synthesized in a similar fashion to **1**, replacing *trans*-oxotrichlorobis(triphenylphosphine)rhenium(V) by the bromo-equivalent. The reaction between 4-ferrocenylaniline and *trans*-$[ReOBr_3(PPh_3)_2]$ was appreciably slower than that for compound **1** indicating that the less electronegative and more bulky bromine atoms exert a retarding effect on the reaction. As with compound **1**, **2** was purified by passing it through a column of silica gel. It was eluted with diethyl ether as a red band and this again yielded a blue-green solid after evaporation of the solvent. The solubility characteristics of **2** were similar to those of **1**. It was very soluble in cold dichloromethane but relatively insoluble in cold diethyl ether. This solubility trend was however reversed on the silica gel column; elution of **2** occurred readily with diethyl ether and hardly at all with dichloromethane. It is interesting to compare the ^1H NMR spectrum of **2** with that of **1**. The chemical shift values of the cyclopentadienyl protons for both complexes are very similar indicating that the resonances of the cyclopentadienyl protons are not very sensitive to alterations in the electronic environment around the rhenium. This can be contrasted with the effects of the ligand exchange on the resonances of the aromatic phenyl moiety in the ferrocenylphenyl group [6.83 and 6.78 ppm (2 × d) for **1** *versus* a singlet at 6.70 ppm for **2**].

X-Ray crystal structure of *trans*-[(4-ferrocenylphenylimido)]-tribromobis(triphenylphosphine)rhenium(V) (2)

Suitable crystals of $\mathbf{2}\cdot CH_2Cl_2$ were again grown using the solvent combination dichloromethane–hexane. The ZORTEP structure of **2** is shown in Fig. 5. A selection of bond lengths and angles are provided in Table 1. A comparison of the bond lengths and angles for **2** with those of **1** indicates that exchanging the chloro substituents for bromo substituents has little effect on the overall geometry of the molecule. Compounds **1** and **2** were prepared from the respective *trans*-oxotrihalobis(triphenylphosphine)rhenium(V) derivatives. $[ReOCl_3(PPh_3)_2]$ has been used extensively in the preparation of rhenium(V) compounds and in the preparation of rhenium compounds in other oxidation states.[9] In view of our interest in ferrocenyl–rhenium compounds, it was decided to replace the two triphenylphosphine ligands in $[ReOCl_3(PPh_3)_2]$ by 1,1′-bis(diphenylphosphine)ferrocene (dppf), a compound that has found wide application in organic synthesis (in cross-coupling reactions for example), coordination chemistry and catalysis.[1]

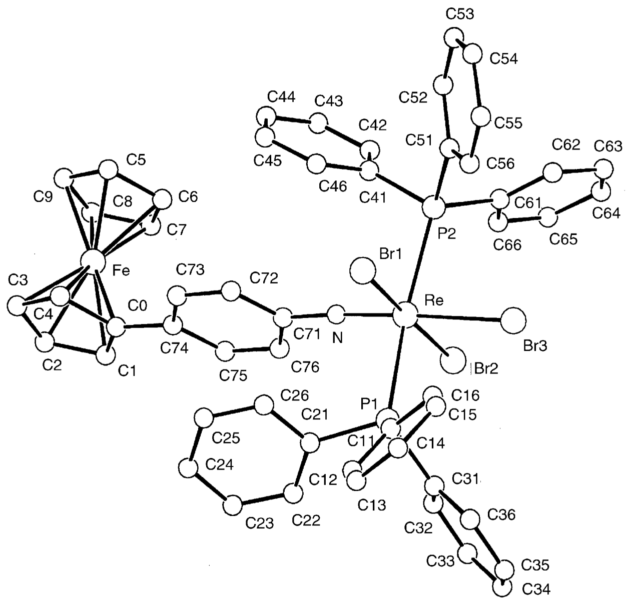


Fig. 5 Molecular structure of **2** with numbering scheme.

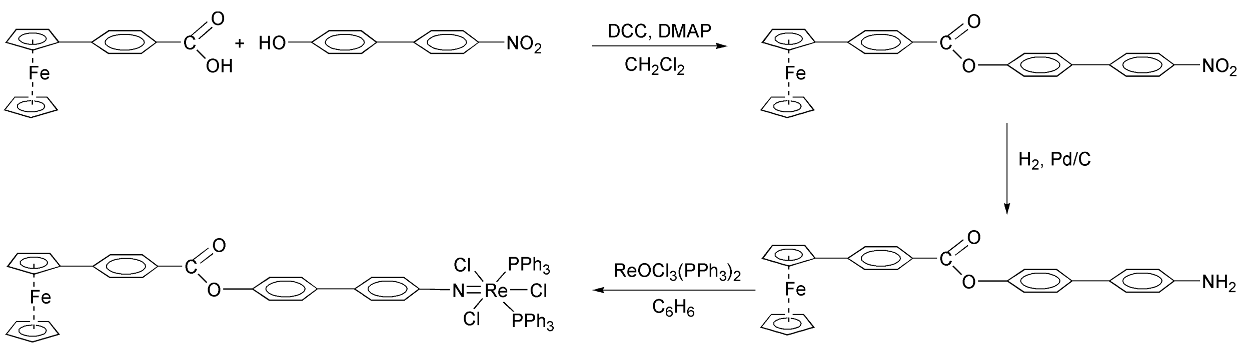
Preparation of *fac*-oxotrichloro[1,1′-bis(diphenylphosphine)-ferrocene]rhenium(V)

The reaction of 1,1′-bis(diphenylphosphine)ferrocene with ammonium perrhenate in the presence of HCl provided *fac*-oxotrichloro[1,1′-bis(diphenylphosphine)ferrocene]rhenium(V) **3** in good yield as dark green crystals. Alternatively, **3** was also obtained by the reaction of 1,1′-bis(diphenylphosphine)-ferrocene with $[ReOCl_3(PPh_3)_2]$. This method is similar to the one recently described by Knoesen *et al.*[5] except that in our method, heating the reaction is avoided. This reaction has been repeated several times and yields have been consistently high (in the range 80–90%) compared to the low yield reported by Knoesen *et al.* (36%). It is also interesting to compare the NMR data obtained for **3** by us with that obtained by Knoesen *et al.* In our case, the ^{31}P chemical shift in $CDCl_3$ is at −25.32 ppm whereas Knoesen *et al.* report a ^{31}P chemical shift at 20.7 ppm in acetone-d_6. The IR spectrum for **3** shows a strong band at 960 cm^{-1} which is indicative of the Re=O bond (Re=O bond distances in compounds of the type $ReOCl_3(PR_3)_2$ available in ESI†).

The reaction of **3** with 4-ferrocenylaniline provided the imido-compound **4** containing two ferrocenyl groups. This compound was again easily purified by passing it through a column of silica gel. Attempts to grow crystals of this material suitable for X-ray analysis have so far failed. The infrared spectrum of the compound shows a band at 1087 cm^{-1} indicative of the Re=N bond. The NMR spectra of the compound (^1H, ^{31}P) are consistent with its structure.

Preparation of complexes 5 and 6

With a view to synthesizing ferrocenomesogens containing the terminal rhenium moiety, complexes **5** and **6** were synthesized, in which the section of the complex containing the ferrocenylphenyl unit was extended. For complex **5**, 4-ferrocenylbenzoic acid was coupled with 4-nitrophenol using dicyclohexylcarbodiimide (DCC) and the resulting nitro derivative was reduced to the amine using catalytic hydrogenation. The amine was reacted with *trans*-oxotrichlorobis(triphenylphosphine)rhenium(V) in benzene in a similar fashion as for the synthesis of **1**. The product was again purified by column chromatography on silica gel and in this case, the colour of the product was noticeably



Scheme 2 Preparation of complex **6**.

different to that of **1** and **2**, being a yellow-brown colour as compared to a blue-green colour. Complex **5** was characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and by IR and FAB mass spectrometry and the data are consistent with its structure. The melting behaviour of **5** was normal and no liquid crystal phases were observed during the heating or cooling of the molecule.

We considered that it could be of interest to invert the ester functional group in complex **5** since this should give rise to a different electron flow along the molecule. To this end, 4-ferrocenylphenol was coupled with 4-nitrobenzoic acid again using DCC and the resulting nitro derivative was reduced to the amine using catalytic hydrogenation. Attempted reaction of the amine with *trans*-oxotrichlorobis(triphenylphosphine)rhenium(V) failed and only the starting materials were recovered after several hours of heating the mixture under reflux in benzene. Reversal of the ester grouping would clearly make the amine funtionality less nucleophilic and hence less reactive but the total lack of reactivity was a surprise. The synthesis of complex **6** is outlined in Scheme 2. 4-Ferrocenylbenzoic acid was coupled with 4-hydroxy-4′-nitrobiphenyl using typical DCC conditions. The nitro compound was obtained in very good yield and was then reduced to the amine using catalytic hydrogenation. The nitro derivative decomposed before melting at temperatures above 260 °C. The amine melted at 235 °C and did not show any abnormal melting characteristics on the heating cycle. On the cooling cycle however, it appeared to exhibit a very short liquid crystal phase just at the point of crystallization. Reaction of the amine with *trans*-oxotrichlorobis(triphenylphosphine)-rhenium(V) in benzene provided complex **6** in a low yield. The complex was characterized by ^{1}H, ^{13}C, ^{31}P NMR spectroscopy, IR and FAB mass spectrometry. Again the complex exhibited normal melting behaviour. Future studies will investigate the effect of introducing extended alkyl chains into the tertiary phosphine groups around rhenium.

Electronic spectral studies

Electronic spectra were recorded in dichloromethane solution for complexes **1**, **2** and **5** and data are presented in Table 3 along with data for simple monoferrocenes. The spectra are represented graphically in Fig. 6. There is a marked bathochromic shift of the longer wavelength absorption on increasing the resonance interaction or electron flow from the ferrocenyl moiety. This is highlighted by comparing the results for 4-ferrocenylaniline and 4-nitrophenylferrocene. The longer wavelength absorptions are 449 nm (356 mol^{-1} dm^{3} cm^{-1}) and 510 nm (2073 mol^{-1} dm^{3} cm^{-1}) respectively. This type of resonance interaction of ferrocene with substrates has been observed before with for example ferrocenylazobenzenes.[10] Complexes **1** and **2** show a long wavelength absorption at 577 nm and 589 nm respectively clearly suggesting a strong resonance effect from the ferrocenyl group towards rhenium. It is interesting to compare the spectra of **1** and **2** with that of **5**. In **5**, the conjugation from the ferrocenyl group towards rhenium is disrupted by the introduction of the ester group and this is

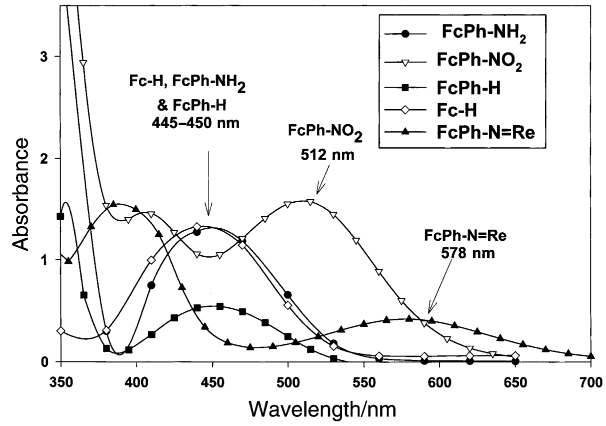


Fig. 6 UV-Visible spectra for ferrocenyl derivatives.

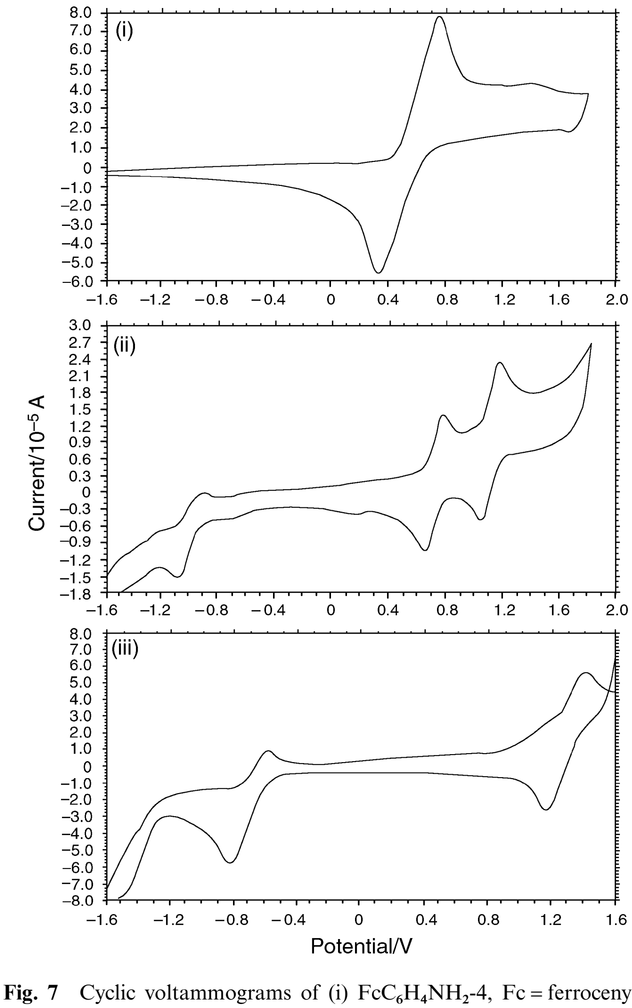


Fig. 7 Cyclic voltammograms of (i) $FcC_6H_4NH_2$-4, Fc = ferrocenyl, (ii) **1** and (iii) $[ReCl_3(NC_6H_4CO_2Me)(PPh_3)_2]$.

Table 3 Electronic spectra of compounds **1**, **2** and **5** compared with those of simple ferrocenes

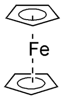
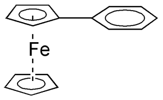
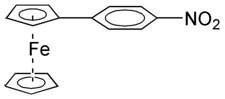
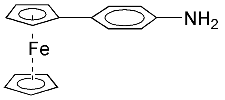
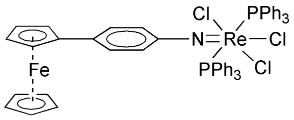
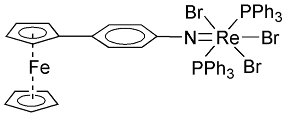
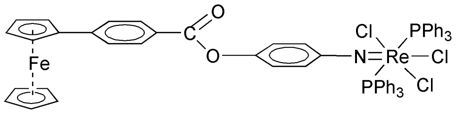
Compound	Structure of compound	λ_{max}/nm (ε_{max}/mol^{-1} dm^3 cm^{-1})
		328 (47), 444 (72)
		450 (182)
		406 (1918), 510 (2073)
		449 (356)
1		388 (22 483), 577 (5695)
2		394 (14 201), 589 (4593)
5		462 (192)

Table 4 Cyclic voltammetry data[a]

Complex	Fe centred process/V	Re centred process	
		Oxidation[b]/V	Reduction[b]/V
$[(C_5H_5)_2Fe]$	+0.44r	—	—
$[(C_5H_5)Fe(C_5H_4C_6H_4NH_2\text{-}4)]$	+0.33r	—	—
$[(C_5H_5)Fe(C_5H_4C_6H_4NO_2\text{-}4)]$	+0.58r	—	—
$[ReCl_3(NPh)(PPh_3)_2]$	—	+0.86qr	−1.23i
$[ReCl_3(NC_6H_4COOMe\text{-}4)(PPh_3)_2]$	—	Not observed	−0.91i
$[ReCl_3(NC_6H_4Fc)(PPh_3)_2]$ **1**	+0.40r	+0.89qr	−1.27i
$[ReBr_3(NC_6H_4Fc)(PPh_3)_2]$ **2**	+0.40r	+0.87qr	−1.24i

[a] Recorded in dichloromethane with a vitreous carbon working electrode, 0.2 M tetrabutylammonium tetrafluoroborate as supporting electrolyte, scan rate 0.4 V s^{-1}. [b] Potentials quoted relative to SCE, r = reversible, qr = quasi reversible, i = irreversible. E_0 quoted for reversible, E_P for irreversible processes.

reflected in the hypsochromic shift of the long wavelength absorbance.

Electrochemical studies

The electrochemical properties of complexes **1** and **2** and related rhenium imido-complexes and ferrocene derivatives were investigated in dichloromethane solution by cyclic voltammetry and the results are given in Table 4. A vitreous carbon working and Pt wire auxiliary electrode and a silver wire pseudo reference electrode were used with 0.2 M $[Bu^n_4N^+][BF_4^-]$ as supporting electrolyte over a range of scan rates. The results are summarized in Table 4. Potentials are corrected to the SCE by use of the ferrocene–ferrocenium couple as internal standard (taken as +0.44 V). Typical cyclic voltammograms for the oxidation of complex **1** and for the reduction of $[ReCl_3(NC_6H_4CO_2Me)(PPh_3)_2]$ are shown in Fig. 7. The voltage scale in the figure is relative to the silver pseudo electrode.

The results for the ferrocenyl derivatives clearly show the effect of the introduction of the electron-withdrawing $C_6H_4NO_2$-4 group in increasing the oxidation potential from the value for ferrocene. Conversely, the introduction of the electron-donating NH_2 group lowers the reduction potential significantly. The cyclic voltammograms of the complexes $[ReCl_3(NC_6H_4R\text{-}4)(PPh_3)_2]$ (R = H, CO_2Me) show a quasi reversible reduction step at *ca.* −1 V due to the formation of the Re(IV) imide species. This becomes more reversible at faster scan rates, consistent with an electrochemical–chemical (EC) mechanism. It is probable that the chemical step following reduction involves loss of chloride. The presence of the electron-withdrawing CO_2Me group as expected causes the reduction to shift to less negative potentials. The oxidation for the unsubstituted imide occurs at +0.86 V and is reversible at all scan rates investigated, as assessed by i_{pa}/i_{pc} ratios close to unity and a linear plot for peak current *versus* scan rate$^{1/2}$. The oxidation process for the CO_2Me derivative was not observed, perhaps because it has been shifted outside the accessible potential window.

The data for the Re–Fe complexes **1** and **2** shows that the Fe and Re centred potentials are relatively little shifted from the values for the Fe and Re complexes individually. In fact, the effect of the Re imide group is smaller than that of the NH_2 and NO_2 groups discussed above. In view of the substituent effects observed above, it seems unlikely that there is a significant electronic communication between the Re and Fe centres. It may be the case that the electron density is balanced in such a way that there is no significant shift from one metal to the other.

Conclusions

We have reported on the synthesis of the first examples of ferrocenyl derivatives in which the ferrocenyl groups are conjugated to rhenium through a nitrogen multiple bond. The results from the X-ray crystal structure determination of the compounds and the NMR chemical shifts provide little evidence for significant electron flow from the ferrocenyl group towards the rhenium atom. The results of the UV/vis spectroscopy and cyclic voltammetry are not conclusive on the issue of the extent of conjugation between the ferrocenyl group and rhenium.

Experimental

Infrared spectra were recorded using a Nicolet Magna 550 Fourier Transform spectrometer as KBr discs. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on either a Varian Unity Plus (500 MHz) spectrometer (Oxford University) or a Bruker AX (300 MHz) (University of Port Elizabeth) at room temperature. The spectra were run in deuteriochloroform using tetramethylsilane as internal standard for ^1H and ^{13}C NMR and phosphoric acid as an external standard for the ^{31}P NMR. UV-Visible spectra were run in dichloromethane on a Shimadzu UV spectrometer. Melting points were recorded using either a Reichert hot stage apparatus (Oxford University) or an Electrothermal IA 900 series digital apparatus (UPE). The melting characteristics of the new compounds were also determined by DSC on a Dupont 2000 calorimeter. X-Ray crystallography determinations were performed at the Inorganic Chemistry Laboratory, University of Oxford, England. Mass spectra were determined on either a Micromass Autospec 500 OAT or a Micromass BIOQ-II Triple Quadrupole ESI mass spectrometer (University of Oxford) or on a VG-70 SEQ/MSS-MS2 at the Cape Technikon, South Africa. 4-Nitrophenylferrocene was prepared by the reaction of 4-nitrobenzenediazonium chloride and ferrocene.[11] *trans*-Oxotrichlorobis(triphenylphosphine)-rhenium(v) was prepared by the method described by Chatt and Rowe.[12] 4-Hydroxy-4′-nitrobiphenyl was supplied by Frinton Laboratories, USA and was used without further purification. 4-Ferrocenylaniline was synthesized by the reduction of 4-nitrophenylferrocene,[13] 4-ferrocenylphenol was synthesized by the diazonium method[14] as was 4-ferrocenylbenzoic acid.[15] Spectroscopic details for these compounds are provided as ESI.†

Syntheses

4-Nitrophenyl-4′-ferrocenyl benzoate. A solution of 4-ferrocenylbenzoic acid (1.00 g, 3.0 mmol), 4-nitrophenol (0.42 g, 3.0 mmol) and 4-dimethylaminopyridine (0.35 g, 3.0 mmol) in anhydrous dichloromethane (200 cm^3) was prepared under an atmosphere of dry nitrogen. A solution of dicyclohexylcarbodiimide (0.28 g, 1.0 mmol) in anhydrous dichloromethane (50 cm^3) was then added slowly over 3 min and the solution stirred at room temperature for 72 h. The solution was then filtered and the solvent removed *in vacuo*. The crude product was purified by flash chromatography on aluminium oxide (neutral) using a mixture of diethyl ether–dichloromethane (1 : 1) as the eluant. The solvent was removed from the collected fractions and a red solid was obtained which was recrystallized from methanol–dichloromethane (0.71 g, 63%), mp 198–200 °C; ν_{max} (KBr) 3108, 1721, 1604, 1596, 1524, 1422, 1349, 1270, 1218, 1185, 1086, 1066, 1034, 1015, 882, 813, 770, 750, 698, 527, 489 cm^{-1}; δ_H ($CDCl_3$) 8.34 (2H, d, *J* 9.1, ArH), 8.10 (2H, d, *J* 8.5, ArH), 7.60 (2H, d, *J* 8.5, ArH), 7.43 (2H, d, *J* 8.5, ArH), 4.76 (2H, t, *J* 1.8, C_5H_4), 4.44 (2H, t, *J* 1.8 Hz, C_5H_4), 4.06 (5H, s, C_5H_5); δ_C ($CDCl_3$) 156.3, 147.5, 145.7, 130.9, 126.3, 125.8, 125.6, 123.0, 96.5, 83.1, 70.3, 67.4; *m*/*z* (εI) 428 (28), 427 (M^+, 100), 277 (45), 249 (13), 121 (44) (Found: M^+, 427.0511; $C_{23}H_{17}FeNO_4$ requires M^+, 427.05034).

4-Aminophenyl-4′-ferrocenyl benzoate. A mixture of 4-nitrophenyl-4′-ferrocenyl benzoate (0.4 g, 1.0 mmol), 10% Pd/C (0.25 g) and anhydrous THF (400 cm^3) was stirred under hydrogen in a Parr hydrogenation reactor for 48 h. The solution was then filtered through Celite and concentrated to leave an orange crystalline material which was recrystallized from dichloromethane–methanol (0.32 g, 81%), mp 199 °C; ν_{max} (KBr) 3443, 1720, 1617, 1511, 1429, 1275, 1229, 1203, 1021, 864, 826, 776, 707, 650, 525 cm^{-1}; δ_H ($CDCl_3$) 8.09 (2H, d, *J* 8.5, ArH), 7.57 (2H, d, *J* 8.5, ArH), 7.01 (2H, d, *J* 8.7, ArH), 6.72 (2H, d, *J* 8.7, ArH), 4.74 (2H, t, *J* 1.8, C_5H_4), 4.41 (2H, t, *J* 1.8 Hz, C_5H_4), 4.05 (5H, s, C_5H_5); δ_C ($CDCl_3$) 165.7, 145.8, 144.1, 143.2, 130.2, 126.9, 125.7, 122.3, 115.7, 96.1, 83.2, 69.9, 66.9; *m*/*z* (εI) 398 (16), 289 (41), 262 (20), 261 (100), 139 (13) (Found: C, 69.4; H, 4.6; N, 3.5; M^+, 397.07699. $C_{23}H_{19}NO_2Fe$ requires C, 69.6; H, 4.8; N, 3.5%; M^+, 397.07652).

4-Nitrobiphenyl-4′-ferrocenyl benzoate. A solution of 4-ferrocenylbenzoic acid (1.57 g, 5.11 mmol), 4′-hydroxy-4-nitrobiphenyl (1.10 g, 5.11 mmol) and 4-dimethylaminopyridine (0.624 g, 5.11 mmol) in anhydrous dichloromethane (150 cm^3) was prepared under an atmosphere of dry nitrogen. A solution of dicyclohexylcarbodiimide (0.352 g, 1.7 mmol) in anhydrous dichloromethane (10 cm^3) was then added slowly over 3 min and the solution stirred at room temperature for 72 h. The solution was then filtered and the solvent removed *in vacuo*. The crude product was purified by flash chromatography on silica gel using a mixture of diethyl ether–dichloromethane (1 : 1) as the eluant. The solvent was removed from the collected fractions and a red solid was obtained which was recrystallized from methanol–dichloromethane (1.51 g, 59%), mp 264–265 °C dec.; ν_{max} (KBr) 3081, 1723, 1603, 1513, 1484, 1342, 1268, 1188, 1068, 1004, 884, 858, 769, 699 cm^{-1}; δ_H ($CDCl_3$) 8.32 (2H, d, *J* 8.8, ArH), 8.13 (2H, d, *J* 8.4, ArH), 7.76 (2H, d, *J* 8.8, ArH), 7.69 (2H, d, *J* 8.6, ArH), 7.60 (2H, d, *J* 8.4, ArH), 7.38 (2H, d, *J* 8.6, ArH), 4.77 (2H, t, *J* 1.8, C_5H_4), 4.44 (2H, t, *J* 1.8 Hz, C_5H_4), 4.07 (5H, s, C_5H_5); δ_C ($CDCl_3$) 165.09, 151.80, 147.17, 146.82, 146.48, 136.42, 130.42, 128.58, 127.80, 126.20, 125.82, 124.20, 122.62, 82.95, 70.08, 69.93, 67.03; *m*/*z* (εI) 505 (6), 504 (31), 503 (M^+, 91), 502 (2), 501 (6), 487 (5), 290 (5), 289 (24), 262 (20), 261 (100), 260 (6), 259 (7), 205 (9), 203 (4), 144 (14), 139 (15), 121 (4) (Found: C, 69.4; H, 4.3; N, 2.7; M^+, 503.08338. $C_{29}H_{21}FeNO_4$ requires C, 69.2; H, 4.2; N, 2.8%; M^+, 503.07473).

4-Aminobiphenyl-4′-ferrocenyl benzoate. A mixture of 4-nitrobiphenyl-4′-ferrocenyl benzoate (320 mg, 0.636 mmol), 10% Pd/C (250 mg) and anhydrous THF (500 cm^3) was stirred under hydrogen in a Parr hydrogenation reactor for 48 h. The solution was then filtered through Celite and concentrated to leave an orange crystalline material which was recrystallized from dichloromethane–methanol (180 mg, 68%), mp 231–233 °C; ν_{max} (KBr) 3444, 3368, 3076, 3036, 2923, 1725, 1606, 1496, 1420, 1272, 1213, 1182, 1089, 1072, 1002, 878, 856, 806, 770, 700, 643, 507 cm^{-1}; δ_H ($CDCl_3$) 8.13 (2H, d, *J* 8.4, ArH), 7.59 (2H, d, *J* 8.5, ArH), 7.58 (2H, d, *J* 8.7, ArH), 7.25 (2H, d, *J* 8.6, ArH), 6.77 (2H, d, *J* 8.4, ArH), 4.75 (2H, t, *J* 1.8, C_5H_4), 4.42 (2H, t, *J* 1.8 Hz, C_5H_4), 4.06 (5H, s, C_5H_5), 3.76 [2H, s (broad), NH_2]; δ_C ($CDCl_3$) 165.74, 150.11, 146.45, 146.28, 139.34, 131.25, 130.75, 128.42, 127.79, 127.05, 126.16, 122.28, 115.81, 83.51, 70.35, 70.29, 67.38; *m*/*z* (εI) 475 (5), 474 (26), 473 (M^+, 76), 290 (7), 289 (36), 262 (19), 261 (100), 260 (6), 259 (7), 205 (8), 185 (5), 184 (6), 139 (11) (Found: C, 73.6; H, 5.1; N, 2.8; M^+, 473.10750. $C_{29}H_{23}FeNO_2$ requires C, 73.6; H, 4.9; N, 2.9%; M^+, 473.10782).

[(4-Ferrocenylphenylimido)]trichlorobis(triphenylphosphine)-rhenium(v) (1). 4-Ferrocenylaniline (110 mg, 0.40 mmol) and *trans*-oxotrichlorobis(triphenylphosphine)rhenium(v) (219 mg, 0.26 mmol) were added to anhydrous benzene (40 cm^3) and this solution was heated under reflux for 8 h. The colour of the solution turned from an orange to a blue very rapidly. After 8 h, the solvent was removed *in vacuo* to leave a dark blue oil which was dissolved in dichloromethane and this solution was passed through a column of silica gel. A red fraction was removed from the column using diethyl ether as eluant, which on removing the solvent left a dark blue solid. Recrystallization from dichloromethane–hexane afforded dark blue-green crystals (134 mg, 44%), mp 276 °C dec.; ν_{max} (KBr) 3060, 1586, 1483, 1434, 1356, 1172, 1092, 745, 694, 518, 494, 298 cm^{-1}; δ_H ($CDCl_3$) 7.80 (12H, m, ArH), 7.26 (18H, m, ArH), 6.83 (2H, d, *J* 8.5, ArH), 6.78 (2H, d, *J* 8.5, ArH), 5.30 (2H, s, CH_2Cl_2), 4.61 (2H, t, *J* 1.8, C_5H_4), 4.45 (2H, t, *J* 1.8 Hz, C_5H_4), 3.99 (5H, s, C_5H_5); δ_C ($CDCl_3$) 134.96, 131.24, 129.96, 127.61, 125.59, 121.75, 82.88, 70.72, 70.16, 67.90, 66.83; δ_P ($CDCl_3$) −19.26 (2P, s, PPh_3); *m*/*z* (FAB) 1057 ($M^+ - Cl$), 1056, 1023 ($M^+ - 2Cl$) (Found: C, 53.4; H, 3.8; N, 1.3. $C_{53}H_{45}Cl_5FeNP_2Re$ requires C, 54.1; H, 3.8; N, 1.2%).

[(4-Ferrocenylphenylimido)]tribromobis(triphenylphosphine)-rhenium(v) (2). 4-Ferrocenylaniline (150 mg, 0.50 mmol) and *trans*-oxotribromobis(triphenylphosphine)rhenium(v) (500 mg, 0.50 mmol) were added to anhydrous benzene (40 cm^3) and this solution was heated under reflux for 12 h. The colour of the solution changed from an orange to a blue-purple during the reaction. After 12 h, the solvent was removed *in vacuo* to leave a dark blue oil which was dissolved in dichloromethane. This solution was filtered through silica gel and then passed through a column of silica gel. A red fraction was eluted with diethyl ether, which on removing the solvent left a dark blue solid. Recrystallization from dichloromethane–hexane afforded dark green crystals (312 mg, 48%), mp 190 °C; ν_{max} (KBr) 3057, 1601, 1585, 1503, 1487, 1437, 1387, 1357, 1292, 1272, 1198, 1178, 1113, 1038, 1023, 889, 859, 834, 754, 704, 564, 525 cm^{-1}; δ_H ($CDCl_3$) 7.92 (12H, m, ArH), 7.22 (18H, m, ArH), 6.70 (4H, s, ArH), 5.30 (2H, s, CH_2Cl_2), 4.61 (2H, t, *J* 1.8, C_5H_4), 4.47 (2H, t, *J* 1.8 Hz, C_5H_4), 4.02 (5H, s, C_5H_5); δ_C ($CDCl_3$) 139.59, 128.70, 126.87, 126.54, 126.30, 69.96, 69.25, 66.89, 62.31; δ_P ($CDCl_3$) −26.71 (2P, s, PPh_3); *m*/*z* (FAB) 1146 ($M^+ - Br$) (Found: C, 49.4; H, 3.3; N, 1.06. $C_{53}H_{45}Br_3Cl_2FeNP_2Re$ requires C, 48.6; H, 3.5; N, 1.07%).

(4-Ferrocenylbenzoatephenylimido)trichlorobis(triphenyl-phosphine)rhenium(v) (5). 4-Aminophenyl-4′-ferrocenyl benzoate (0.13 g, 3.0 mmol) and *trans*-oxotrichlorobis(triphenylphosphine)rhenium(v) (0.27 g, 3.0 mmol) were added to anhydrous benzene (40 cm^3) and this solution was heated under reflux for 12 h. The colour of the solution changed from orange to brown. The solution was concentrated and passed through a column of silica gel. Diethyl ether was used to elute a red fraction and upon concentration, a brown solid was obtained. Recrystallization from dichloromethane–hexane afforded a yellow-brown needle-like solid (0.21 g, 56%), mp 288 °C dec.; ν_{max} (KBr) 3051, 1735, 1600, 1588, 1484, 1436, 1261, 1200, 1174, 1110, 1068, 1017, 891, 829, 749, 691, 516, 390, 380 cm^{-1}; δ_H ($CDCl_3$) 8.05 (2H, d, *J* 8.5, ArH), 7.82 (12H, m, ArH), 7.58 (2H, d, *J* 8.5, ArH), 7.28 (18H, m, ArH), 6.85 (2H, d, *J* 8.8, ArH), 6.64 (2H, d, *J* 8.8, ArH), 4.76 (2H, t, *J* 1.8, C_5H_4), 4.44 (2H, t, *J* 1.8 Hz, C_5H_4), 4.05 (5H, s, C_5H_5); δ_C ($CDCl_3$) 134.9, 134.8, 134.7, 131.6, 131.2, 130.4, 130.1, 127.7, 127.6, 125.8, 126.9, 126.5, 126.3, 70.0, 69.2, 62.3, 66.9; δ_P ($CDCl_3$) −19.9 (2P, s, PPh_3); *m*/*z* (FAB) 1212 (M^+), 1176 ($M^+ - Cl$), 949 ($M^+ - PPh_3$), 913 ($M^+ - [PPh_3 + Cl]$), 878 ($M^+ - [PPh_3 + 2Cl]$) (Found: C, 58.8; H, 3.5; N, 1.12. $C_{59}H_{47}Cl_3FeP_2O_2ReN$ requires C, 58.4; H, 3.9; N, 1.15%).

(4-Ferrocenylbenzoate-1,1-biphenyl-4-imido)trichlorobis-(triphenylphosphine)rhenium(v) (6). 4-Aminobiphenyl-4′-ferrocenyl benzoate (130 mg, 0.27 mmol) and *trans*-oxotrichlorobis(triphenylphosphine)rhenium(v) (230 mg, 0.27 mmol) were added to anhydrous benzene (40 cm^3) and this solution was heated under reflux for 12 h. The colour of the solution changed from orange to brown. The solution was concentrated and passed through a column of silica gel. Diethyl ether was used to elute a red fraction and upon concentration, a brown solid was obtained. Recrystallization from dichloromethane–hexane afforded an orange-brown solid (120 mg, 37%), mp 203 °C dec.; ν_{max} (KBr) 3057, 1731, 1604, 1588, 1482, 1434, 1263, 1207, 1177, 1087, 1065, 1002, 810, 745, 693, 521 cm^{-1}; δ_H ($CDCl_3$) 8.05 (2H, m, ArH), 7.80–7.75 (12H, m, ArH), 7.53 (2H, d, *J* 8.0, ArH), 7.37–7.24 (18H, m, ArH), 7.16 (2H, d, *J* 8.6, ArH), 7.09 (2H, d, *J* 8.4, ArH), 7.02 (2H, d, *J* 8.4, ArH), 6.64 (2H, d, *J* 8.8, ArH), 4.71 (2H, t, *J* 1.8, C_5H_4), 4.41 (2H, t, *J* 1.8 Hz, C_5H_4), 4.04 (5H, s, C_5H_5); δ_P ($CDCl_3$) −16.50 (2P, s, PPh_3); *m*/*z* (FAB) 1288 ($M^+ + H$), 1287 (M^+), 1285 ($M^+ - 2H$), 1252 ($M^+ - Cl$), 1137, 991 (Found: C, 60.5; H, 3.9; N, 1.0. $C_{65}H_{51}Cl_3FeP_2O_2ReN$ requires C, 60.5; H, 4.0; N, 1.1%).

***fac*-Oxotrichloro[1,1′-bis(diphenylphosphine)ferrocene]-rhenium(v) (3) from the reaction of ammonium perrhenate, 1,1′-bis(diphenylphosphine)ferrocene and HCl.** A suspension of ammonium perrhenate (105 mg, 0.39 mmol) in concentrated hydrochloric acid (4 cm^3) was added to an orange suspension of 1,1′-bis(diphenylphosphine)ferrocene (603 mg, 1.09 mmol) in glacial acetic acid (10 cm^3). The mixture was stirred for 30 min under nitrogen after which a green solid was isolated from the mixture. This was washed with diethyl ether (2 × 2 cm^3) and was recrystallized from dichloromethane–hexane to give dark green crystals identified as *fac*-oxotrichloro[1,1′-bis(diphenylphosphine)ferrocene]rhenium(v) (224 mg, 67%), mp 244–246 °C; ν_{max} (KBr) 3051, 1486, 1434, 1389, 1309, 1175, 1150, 1091, 1064, 960, 834, 743, 697, 634, 554, 495, 460, 410, 331, 298, 285 cm^{-1}; δ_H ($CDCl_3$) 7.92 (4H, m, ArH), 7.75 (4H, m, ArH), 7.42 (12H, m, ArH), 5.31 (2H, s, C_5H_4), 4.72 (2H, s, C_5H_4), 4.47 (2H, s, C_5H_4), 4.43 (2H, s, C_5H_4); δ_C ($CDCl_3$) 135.55, 135.49, 135.45, 135.31, 135.25, 135.19, 133.86, 132.57, 131.75, 131.14, 128.83, 128.77, 128.70, 127.77, 127.70, 127.63, 81.23, 80.46, 76.99, 76.66, 75.63, 75.56, 74.08, 73.54; δ_P ($CDCl_3$) −25.32 (2P, s, PPh_2); *m*/*z* (FAB) 826 ($M^+ - Cl$), 791 ($M^+ - 2Cl$), 756 ($M^+ - 3Cl$), 554 ($M^+ - ReOCl_3$) (Found: C, 47.6; H, 3.4. $C_{34}H_{28}Cl_3FeOP_2Re$ requires C, 47.3; H, 3.3%).

***fac*-Oxotrichloro[1,1′-bis(diphenylphosphine)ferrocene]-rhenium(v) (3) from the reaction of *trans*-[$ReOCl_3(PPh_3)_2$] and 1,1′-bis(diphenylphosphine)ferrocene.** The reaction was carried out under an atmosphere of high purity nitrogen. *trans*-[$ReOCl_3(PPh_3)_2$] (114 mg, 0.14 mmol) was added to anhydrous toluene (5 cm^3) to which was also added a solution of 1,1′-bis(diphenylphosphine)ferrocene (78 mg, 0.14 mmol) in anhydrous toluene (5 cm^3). The mixture was stirred at room temperature for 15 h. A green solid was filtered off, washed with toluene (2 cm^3) and diethyl ether (2 cm^3) and dried under vacuum and was finally recrystallized from dichloromethane–hexane, identified as *fac*-oxotrichloro[1,1′-bis(diphenylphosphine)ferrocene]rhenium(v) (97 mg, 80%), characterization as above.

Trichloro(ferrocenylphenylimido)[1,1′-bis(diphenylphosphine)-ferrocene]rhenium(V) (4). 4-Ferrocenylaniline (51 mg, 0.18 mmol) was dissolved in anhydrous benzene (10 cm^3) and this solution was added to a solution of *fac*-oxotrichloro[1,1′-bis(diphenylphosphine)ferrocene]rhenium(V) (103 mg, 0.12 mmol) in anhydrous benzene (10 cm^3) and the mixture was heated under reflux for 24 h. During that time, the solution changed colour from green to dark red and finally to deep purple. Evaporation of the solvent left a blue oily residue which upon addition of dichloromethane followed by hexane provided a green solid. The latter was washed with hexane (2 × 2 cm^3), dried *in vacuo* and then passed through a column of silica gel. Dichloromethane was used to elute a dark red band which on removing the solvent *in vacuo* left a dark solid. This was recrystallized from dichloromethane–hexane and identified as trichloro(ferrocenylphenylimido)[1,1′-bis-(diphenylphosphine)ferrocene]rhenium(V) (**4**) (19 mg, 14%), mp 295 °C dec.; ν_{max} (KBr) 1653, 1588, 1483, 1434, 1331, 1165, 1087, 1029, 914, 886, 840, 743, 694, 546, 518, 494, 473 cm^{-1}; δ_H (CDCl$_3$) 8.00 (4H, m, ArH), 7.85 (4H, m, ArH), 7.32–7.06 (12H, m, ArH), 6.84 (2H, d, *J* 8.6, ArH), 6.63 (2H, d, *J* 8.5, ArH), 5.28 (2H, s, C$_5$H$_4$), 4.67 (2H, s, C$_5$H$_4$), 4.64 (2H, s, C$_5$H$_4$), 4.59 (4H, m, C$_5$H$_4$), 4.43 (2H, t, *J* 1.7 Hz, C$_5$H$_4$), 4.01 (5H, s, C$_5$H$_5$); δ_P (CDCl$_3$) −16.29; *m*/*z* (FAB) 1122 (M$^+$ + H), 1121 (M$^+$), 1083 (M$^+$ − Cl), 1052 (M$^+$ − 2Cl) (Found: C, 52.6; H, 3.8; N, 1.2. $C_{50}H_{41}Cl_3Fe_2NP_2Re$ requires C, 53.5; H, 3.7; N, 1.2%).

Trichloro(4-imidophenyl-4′-ferrocenyl benzoate)[1,1′-bis-(diphenylphosphine)ferrocene]rhenium(V) (7). 4-Aminophenyl-4′-ferrocenyl benzoate (185 mg, 0.47 mmol) was dissolved in anhydrous benzene (10 cm^3) and this solution was added to a solution of *fac*-oxotrichloro[1,1′-bis(diphenylphosphine)-ferrocene]rhenium(V) (403 mg, 0.47 mmol) in anhydrous benzene (10 cm^3) and the mixture was heated under reflux for 72 h. During that time, the solution changed colour from green to dark red and finally to brown. Evaporation of the solvent left a dark brown residue. The latter was washed with hexane (2 × 2 cm^3), dried *in vacuo* and then passed through a short silica gel column. Dichloromethane was used to elute a dark red band which on removing the solvent *in vacuo* left a brown solid. This was recrystallized from dichloromethane–hexane to give a light brown solid identified as trichloro(4-imidophenyl-4′-ferrocenyl benzoate)[1,1′-bis(diphenylphosphine)ferrocene]rhenium(V) (221 mg, 39%), mp 265 °C dec.; ν_{max} (KBr) 1731, 1605, 1583, 1480, 1434, 1257, 1203, 1171, 1158, 1086, 1051, 1011, 890, 821, 746, 697, 632, 547, 518 cm^{-1}; δ_H (CDCl$_3$) 8.02 (8H, m, ArH), 7.80 (8H, m, ArH), 7.58 (2H, d, *J* 8.4, ArH), 7.34–7.08 (6H, m, ArH), 6.69 (2H, d, *J* 9.1, ArH), 6.65 (2H, d, *J* 9.1, ArH), 5.26 (2H, s, C$_5$H$_4$), 4.76 (2H, s, C$_5$H$_4$), 4.67 (4H, s, C$_5$H$_4$), 4.60 (2H, m, C$_5$H$_4$), 4.45 (2H, t, *J* 1.7 Hz, C$_5$H$_4$), 4.06 (5H, s, C$_5$H$_5$); δ_P (CDCl$_3$) −16.64; *m*/*z* (FAB) 1242 (M$^+$ + 2H), 1241 (M$^+$ + H), 1240 (M$^+$), 1206 (M$^+$ − Cl), 866, 773 (Found: C, 54.3; H, 3.7; N, 1.0. $C_{57}H_{45}Cl_3Fe_2NO_2P_2Re$ requires C, 55.2; H, 3.7; N, 1.1%).

Structure analysis and refinement for compounds 1, 2

Intensity data were collected on an Enraf-Nonius DIP2000 image-plate diffractometer with monochromated Mo-Kα radiation. The images were processed with the DENZO and SCALEPAK programs.[16] The structures were solved *via* direct methods[17] and refined on F_o^2 by full-matrix least-squares.[18] All non-hydrogen atoms were anisotropic. The hydrogen atoms were included in idealized positions with U_{iso} free to refine. The weighting scheme gave satisfactory agreement with the analyses. Sources of scattering factors were as in ref. 17. The numbering of all the atoms in the structures was produced with ZORTEP.[19] A summary of the X-ray structural data for complexes **1** and **2** is provided in Table 5.

Table 5 Summary of X-ray structural data for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{53}H_{45}Cl_3FeNP_2Re$	$C_{53}H_{45}Br_3Cl_2FeNP_2Re$
M	1177.14	1310.52
a/Å	12.206(2)	12.078(1)
b/Å	13.668(2)	13.615(1)
c/Å	15.585(2)	15.518(1)
α/°	76.617(10)	77.745(3)
β/°	77.650(10)	77.667(3)
γ/°	80.045(10)	79.351(2)
V/Å^3	2418.6(6)	2410.0(3)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
μ(Mo-Kα)/mm^{-1}	3.180	5.512
T/K	150(2)	150(2)
Reflections collected	2941	9060
Independent reflections	2941	9060
Reflections observed	2639	7596
$R1$, $wR2$	0.0727, 0.1645	0.0397, 0.1008

CCDC reference numbers 167710–167712. This includes structural data for compound **3**.

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