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Synthesis, Characterisation, Complexation and Electrochemistry of Linear Tridentate $FcE(CH_2)_3E'(CH_2)_3EFc$ (E, E′ = Se or Te) Ligands: X-ray Crystal Structures of $FcSe(CH_2)_3Se(CH_2)_3SeFc$ and $[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]PF_6$ $\{Fc = [Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)]\}$

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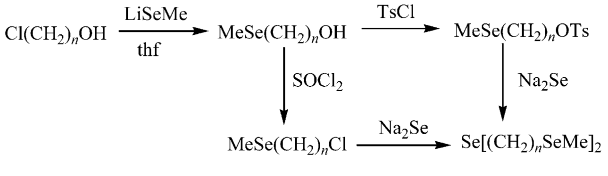
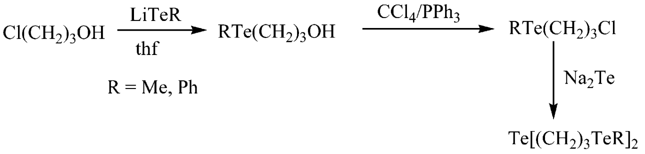
A series of linear tridentate ligands, $FcE(CH_2)_3E'(CH_2)_3EFc$ (E, E′ = Se or Te), was synthesised. Their chloropalladium(II) and chloroplatinum(II) complexes were also prepared. The new compounds were characterised by a range of spectroscopic and analytical techniques, including multinuclear NMR spectrometry and X-ray crystallography. In an electrochemistry study of the complexes no communication between the ferrocenyl centres was observed, regardless of the through-bond Fe···Fe distance.

Introduction

In comparison to the widely investigated linear triphosphanes,[1] far fewer chalcogen analogues have been prepared and studied. Linear tridentate chalcogenide compounds that have previously been reported include $MeS(CH_2)_nS(CH_2)_nSMe$ (n = 2 or 3),[2,3] $MeSe(CH_2)_nSe(CH_2)_nSeMe$ (n = 2 or 3),[3,4] $RS(CH_2)_3S(CH_2)_3SR$ (R = Et, Ph or *i*Pr),[5] $RTe(CH_2)_3Te(CH_2)_3TeR$ (R = Me, Ph)[6] and $MeS(CH_2)_nTe(CH_2)_nSMe$ (n = 2 or 3).[7,8] These compounds have generally been synthesised by similar methods, as shown in Schemes 1 and 2. The common route includes three steps and involves the preparation of Na_2E from Na metal in liquid NH_3; thus, this method is time consuming and requires critical control of conditions.



Scheme 1. Synthetic route to $MeSe(CH_2)_nSe(CH_2)_nSeMe$ (n = 2, 3).



Scheme 2. Synthetic route to $RTe(CH_2)_3Te(CH_2)_3TeR$ (R = Me or Ph).

We previously prepared bis(ferrocenylchalcogeno)alkanes and studied the electronic influence of ferrocenyl substituents in soft ligand systems and metal complexes.[9–11] We wished to extend our systematic study of bis(ferrocenylchalcogeno) derivatives to linear tridentate chalcogenide ligands and their complexes, and in particular to develop a direct and mild route to compounds of this type.

Results and Discussion

Synthesis of $FcE(CH_2)_3E'(CH_2)_3EFc$ (E, E′ = Se or Te)

The mechanism of the synthesis of bis(ferrocenylchalcogeno)alkanes shows that in this nucleophilic substitution reaction, the first FcE^- group easily replaces the leaving group I^-, but the second step is much slower, prompting the idea that by using Br^- instead of I^-, and by performing the reaction at 0 °C, then $FcE(CH_2)_3Br$ could be obtained as the main product. This was confirmed by experiment. First, four equivalents of sodium borohydride were used to reduce the diferrocenyl dichalcogenide in ethanol. After 1 h, the mixture became a clear orange-yellow (E = Se) or red (E = Te) solution. Then at 0 °C, this solution was slowly transfer-

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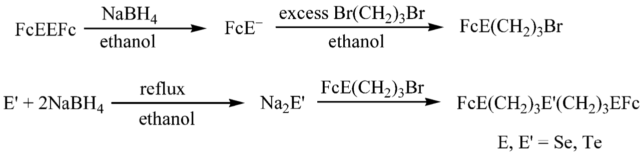
red to a diluted ethanol solution containing an excess amount of 1,3-dibromopropane. The reaction was allowed to continue for 2 h, and the solution colour changed to yellow. After column chromatography the FcE(CH$_2$)$_3$Br product was generally isolated as an orange oil in high yield.

The target linear tridentate compounds, FcE(CH$_2$)$_3$E′(CH$_2$)$_3$EFc, were obtained by the sequence shown in Scheme 3. For example, Se powder and two equivalents of NaBH$_4$ were heated at reflux in degassed ethanol under N$_2$ for 1 h to produce a clear pale-yellow solution of Na$_2$Se. A thf solution of two equivalents of FcSe(CH$_2$)$_3$Br was then added slowly, and the solution was left to stir at room temperature for 12 h. After removing the solvent by evaporation under reduced pressure, the residue was treated with water and then extracted with CH$_2$Cl$_2$. The extract was dried with MgSO$_4$, and the solvents were evaporated to dryness. The residue was then subjected to column chromatography on SiO$_2$ to produce FcSe(CH$_2$)$_3$Se(CH$_2$)$_3$SeFc. The other three compounds FcE(CH$_2$)$_3$E′(CH$_2$)$_3$EFc (E = Se, E′ = Te; E = Te, E′ = Se; E = Te, E′ = Te) could be synthesised similarly.



$$\text{FcEEFc} \xrightarrow[\text{ethanol}]{\text{NaBH}_4} \text{FcE}^- \xrightarrow[\text{ethanol}]{\text{excess Br(CH}_2)_3\text{Br}} \text{FcE(CH}_2)_3\text{Br}$$

$$\text{E}' + 2\text{NaBH}_4 \xrightarrow[\text{ethanol}]{\text{reflux}} \text{Na}_2\text{E}' \xrightarrow{\text{FcE(CH}_2)_3\text{Br}} \text{FcE(CH}_2)_3\text{E}'(\text{CH}_2)_3\text{EFc}$$

E, E′ = Se, Te

Scheme 3. Synthetic scheme for FcE(CH$_2$)$_3$E′(CH$_2$)$_3$EFc.

Synthesis of [MCl{FcE(CH$_2$)$_3$E′(CH$_2$)$_3$EFc}]PF$_6$ (M = Pd or Pt; E, E′ = Se or Te)

The reaction of a linear tridentate ligand with [MCl$_2$(NCMe)$_2$] (M = Pd or Pt) and TlPF$_6$ in a 1:1:1 ratio was previously used to prepare planar cationic complexes of the general formula [MClL]$^+$.[6,8] A similar method was adopted for the synthesis of Pd and Pt complexes of FcE(CH$_2$)$_3$E′(CH$_2$)$_3$EFc (E, E′ = Se, Te). All eight complexes showed multiplet peaks with the correct isotope structure in the mass spectra consistent with the formulation [MCl{FcE(CH$_2$)$_3$E′(CH$_2$)$_3$EFc}]$^+$. For four of the complexes, the carbon and hydrogen contents, as determined by microanalysis, were slightly low, although their ratio was correct. This we ascribe to the difficulty of ensuring complete removal of TlCl.

NMR Spectroscopy

The ^{1}H and ^{13}C NMR spectra of the ligands themselves exhibit the same general trends as those observed for FcE(CH$_2$)$_3$E′Fc.[9] The ^{77}Se NMR and ^{125}Te NMR spectroscopic data for FcE(CH$_2$)$_3$E′(CH$_2$)$_3$EFc show that the FcE groups are too far away to have a significant effect on the central chalcogen atom E′, so that its chemical shift is similar to that in Bu$_2$Se (δ = 167 ppm) or Bu$_2$Te (δ = 228 ppm) for E′ = Se or Te, respectively. Only in FcTe(CH$_2$)$_3$Te(CH$_2$)$_3$TeFc was the coupling resolved between the two types of chalcogen atoms: in this case $^4J_{\text{Te,Te}}$ = 43 Hz.

In contrast to the behaviour of the complexes of the analogous bidentate ligands,[10] the [MCl{FcE(CH$_2$)$_3$E′(CH$_2$)$_3$EFc}]$^+$ species give generally well-resolved NMR spectra at room temperature. The spectra are complicated by the potential presence in solution of pairs of *meso* and DL invertomers.[12] The fluxional processes leading to interconversion of these invertomers are generally slow at room temperature, and only for the palladium complexes was broadening of the peaks in the ^{1}H spectra occasionally observed. In each *meso* invertomer the two ferrocenyl groups are equivalent, but in the NMR-indistinguishable DL invertomers they are not, so that there may be up to four ^{1}H (and ^{13}C) resonances for the unsubstituted cyclopentadienyl rings, whose integration reflects the relative abundance of the invertomers. In practice, one dominant singlet is usually observed, consistent with a *meso* invertomer being the main form in solution. This is in accordance with the structure observed in the solid state (see below). In comparison to the ^{1}H NMR spectra of the ligands, there is a high frequency coordination shift, but this may in part be due to a change in solvent. Separate signals are observed for 2-H and 5-H, and for C-2 and C-5, the C-H groups of the substituted cyclopentadienyl ring, as these are rendered inequivalent on complexation. Similarly, the hydrogen atoms in each pair of CH$_2$ groups are also no longer chemically equivalent, and they give rise to distinct resonances.

The ^{77}Se NMR resonances of [PdCl{FcSe(CH$_2$)$_3$Se(CH$_2$)$_3$SeFc}]PF$_6$ (δ = 202, 227 ppm) and [PtCl{FcSe(CH$_2$)$_3$Se(CH$_2$)$_3$SeFc}]PF$_6$ (δ = 200, 220 ppm) in CD$_3$COCD$_3$ occur at considerably lower field than those of the free ligand FcSe(CH$_2$)$_3$Se(CH$_2$)$_3$SeFc in CDCl$_3$ (δ = 154, 190 ppm). The observation of only one pair of peaks confirms that a *meso* invertomer is predominant. The chemical shift of the terminal selenium atom is always greater than that of the central one, but the difference between them ($\Delta\delta$) becomes smaller upon coordination: 25 and 20 ppm compared to 36 ppm in the free ligand. There is a significant difference between the values of the two platinum–selenium coupling constants in [PtCl{FcSe(CH$_2$)$_3$Se(CH$_2$)$_3$SeFc}]PF$_6$, as $^1J_{\text{Pt,Se}}$ is much greater for the terminal selenium atoms (388 Hz vs. 268 Hz).

As expected, if only a *meso* invertomer is sufficiently abundant to be observed, the ^{77}Se NMR spectra of [MCl{FcSe(CH$_2$)$_3$Te(CH$_2$)$_3$SeFc}]PF$_6$ (M = Pd, Pt) contain just one peak (M = Pd, δ = 195 ppm; M = Pt, δ = 217 ppm) at a similar chemical shift to the resonances for the terminal selenium atoms in the analogous complexes [MCl{FcSe(CH$_2$)$_3$Se(CH$_2$)$_3$SeFc}]PF$_6$ (M = Pd, δ = 202 ppm; M = Pt, δ = 220 ppm). For [PtCl{FcSe(CH$_2$)$_3$Te(CH$_2$)$_3$SeFc}]PF$_6$ the coupling constant between the platinum centre and the terminal selenium atoms was 399 Hz (cf. 388 Hz for [PtCl{FcSe(CH$_2$)$_3$Se(CH$_2$)$_3$SeFc}]PF$_6$).

Two peaks of unequal intensity were observed in the ^{77}Se NMR spectrum of each of the complexes [PdCl{FcTe(CH$_2$)$_3$Se(CH$_2$)$_3$TeFc}]PF$_6$ [δ = 226 (major), 232 (minor) ppm] and [PtCl{FcTe(CH$_2$)$_3$Se(CH$_2$)$_3$TeFc}]PF$_6$ [δ = 204.0 (major), 204.4 (minor) ppm], implying the presence of two invertomers in solution. The ^{125}Te NMR spectrum of the platinum complex (see below) shows that these are the two *meso* forms. The chemical shift difference between the invertomers is larger in the Pd complex. The coupling constant between the platinum centre and the central selenium atom was 187 Hz in the more abundant invertomer of $[PtCl\{FcTe(CH_2)_3Se(CH_2)_3TeFc\}]PF_6$, similar to that in $[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]PF_6$ (268 Hz). The platinum–selenium coupling in the other invertomer was unresolved.

The ^{125}Te NMR spectrum at 300 K of $[PtCl\{FcTe(CH_2)_3Se(CH_2)_3TeFc\}]PF_6$ also showed two sharp resonances at δ = 357.0 ppm (major, $^1J_{Te,Pt}$ = 480 Hz) and 356.7 ppm (minor, platinum coupling unresolved). The observation of only one peak for the less-abundant species shows that this must be the second *meso* invertomer, as the DL pair would give rise to two. In the ^{125}Te NMR spectrum of $[PtCl\{FcTe(CH_2)_3Te(CH_2)_3TeFc\}]PF_6$ three sets of peaks were observed: 355 ppm ($^1J_{Te,Pt}$ = 515 Hz), 354 ppm ($^1J_{Te,Pt}$ = 232 Hz), 369 ppm. The resonance at δ = 355 ppm can be assigned to the terminal tellurium atoms of a *meso* invertomer by comparison with the data for $[PtCl\{FcTe(CH_2)_3Se(CH_2)_3TeFc\}]PF_6$; on the basis of its smaller platinum–tellurium coupling constant, the resonance at δ = 354 ppm is attributed to the central tellurium atom of this species. The value of $\Delta\delta$ between the terminal and central tellurium atoms is only 1 ppm, compared to 66 ppm in the free ligand $FcTe(CH_2)_3Te(CH_2)_3TeFc$. The third resonance at δ = 369 ppm with unresolved platinum satellites is due to the terminal tellurium atoms of the other *meso* invertomer; a resonance for the central tellurium atom in this species was not detected. No peaks were resolved in the ^{125}Te NMR spectra of $[MCl\{FcSe(CH_2)_3Te(CH_2)_3SeFc\}]PF_6$ (M = Pd, Pt), $[PdCl\{FcTe(CH_2)_3Se(CH_2)_3TeFc\}]PF_6$ and $[PdCl\{FcTe(CH_2)_3Te(CH_2)_3TeFc\}]PF_6$, suggesting these complexes are fluxional on the ^{125}Te NMR timescale.

Crystal Structures

Crystals of $FcSe(CH_2)_3Se(CH_2)_3SeFc$ were obtained as orange yellow plates from CH_2Cl_2/hexanes. The compound crystallises in the unusual *F*2*dd* space group of the orthorhombic system. The molecular structure is illustrated in Figure 1 and pertinent bond parameters are collected in Table 1. The symmetry-independent unit consists of one half of the molecule, which possesses twofold rotational symmetry around an axis passing through the central Se atom. The ferrocene sp^2 C–Se bond length [1.896(5) Å] is similar to those in Fc_2Se_2 [1.898(10), 1.904(9) Å][13] and longer than those in $FcSe(CH_2)_3SeFc$ [1.872(6), 1.878(6) Å].[10] The sp^3 C–SeFc bond length is 1.955(4) Å, which is shorter than those in $FcSe(CH_2)_3SeFc$ [1.995(6), 1.979(6) Å], and the middle Se–C bond length is shorter still [1.947(4) Å]. The packing diagram (Figure 2) shows that molecules are aligned parallel to the direction of the *c* crystallographic axis.

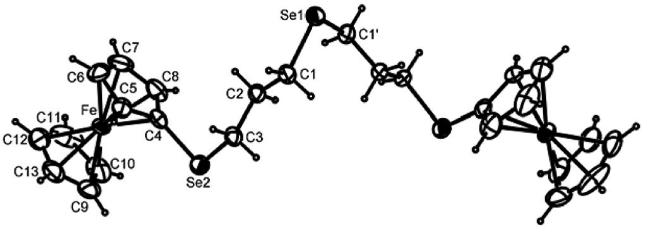


Figure 1. View of the structure of $FcSe(CH_2)_3Se(CH_2)_3SeFc$ with the atomic numbering scheme adopted. The primed atom is related to the corresponding unprimed one through a twofold axis. Thermal ellipsoids are drawn at the 30% probability level.

Table 1. Selected bond lengths and angles for $FcSe(CH_2)_3Se(CH_2)_3SeFc$.[a]

Bond lengths [Å]			
Se1–C1	1.947(4)	Se2–C3	1.955(4)
C1–C2	1.528(6)	Se2–C4	1.896(5)
C2–C3	1.519(7)		
Bond angles [°]			
C1–Se1–C1^i	100.1(3)	C2–C3–Se2	114.0(3)
Se1–C1–C2	115.3(3)	C3–Se2–C4	96.9(2)
C1–C2–C3	110.3(4)	Se2–C4–Fe	124.7(2)
Torsion angles [°]			
C1^i–Se1–C1–C2	–58.0(3)	C2–C3–Se2–C4	–63.8(4)
Se1–C1–C2–C3	–174.8(3)	C3–Se2–C4–Fe	–161.9(3)
C1–C2–C3–Se2	–175.0(3)		

[a] Symmetry code i: *x*, –*y*, 1 – *z*.

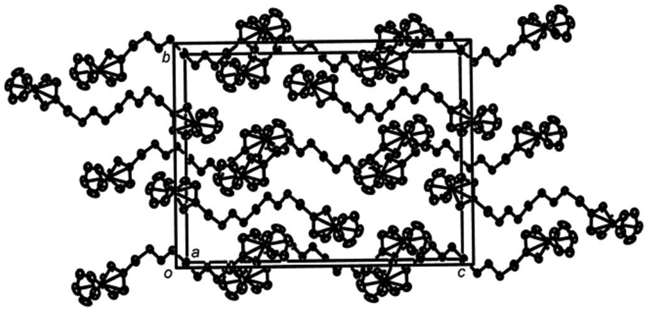


Figure 2. A view of the packing in the structure of $FcSe(CH_2)_3Se(CH_2)_3SeFc$ in proximity of the *bc* face of the unit cell. Hydrogen atoms are omitted for clarity.

$[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]PF_6$ crystallised as orange plates in the monoclinic space group *P*2$_1$/*n*. The structure consists of $[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]^+$ cations and PF_6^- anions. The geometry of the cation is illustrated in Figure 3 and pertinent bond parameters are collected in Table 2. The packing in the structure (Figure 4) is characterised by the presence of pairs of cations related by an inversion centre; these exhibit facing cyclopentadienyl rings, whose centroids lie 3.62 Å apart, and the shortest distance between carbon atoms of the two rings is 3.29(3) Å.

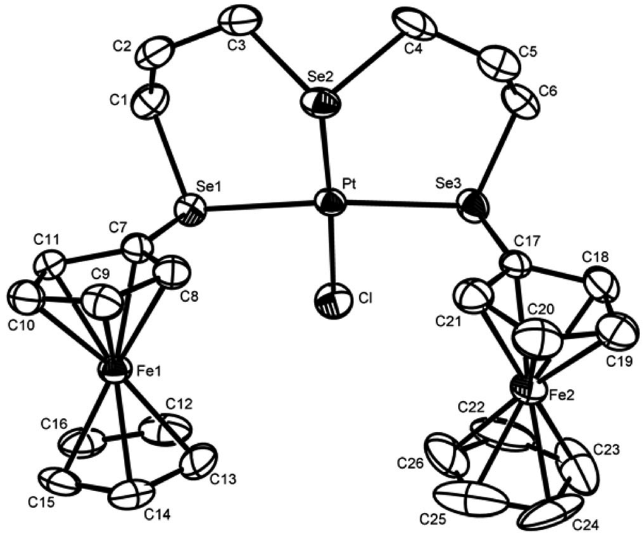


Figure 3. View of the cation in the structure of PtCl{FcSe(CH$_2$)$_3$Se(CH$_2$)$_3$SeFc}]PF$_6$ with the atomic numbering scheme adopted. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

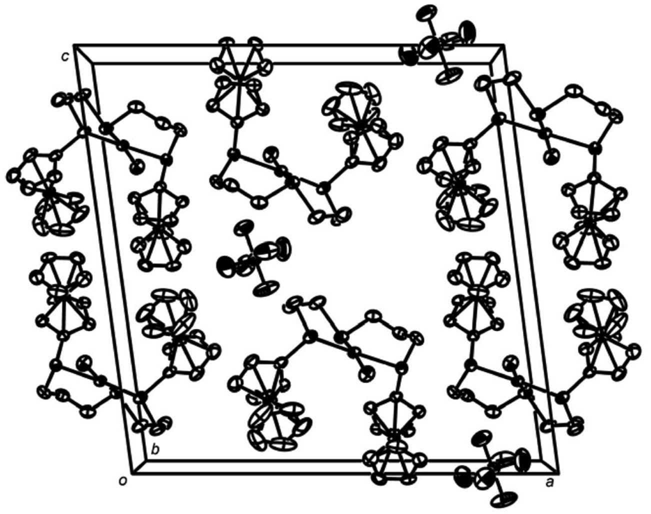


Figure 4. A view of the packing in the structure of [PtCl{FcSe(CH$_2$)$_3$Se(CH$_2$)$_3$SeFc}]PF$_6$ along the *b* crystallographic direction. Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths and angles for [PtCl{FcSe(CH$_2$)$_3$Se(CH$_2$)$_3$SeFc}]PF$_6$.

Bond lengths [Å]					
Pt–Cl	2.316(2)	Se1–C7	1.901(8)	C1–C2	1.49(1)
Pt–Se1	2.4126(9)	Se2–C3	1.959(10)	C2–C3	1.52(1)
Pt–Se2	2.3699(9)	Se2–C4	1.971(9)	C4–C5	1.49(2)
Pt–Se3	2.4158(9)	Se3–C6	1.965(10)	C5–C6	1.50(2)
Se1–C1	1.960(9)	Se3–C17	1.903(9)		

Bond angles [°]			
Cl–Pt–Se2	172.96(7)	Pt–Se1–C7	107.2(2)
Se1–Pt–Se3	167.77(3)	Pt–Se2–C3	108.1(3)
Cl–Pt–Se1	83.90(7)	Pt–Se2–C4	110.1(4)
Cl–Pt–Se3	85.08(7)	Pt–Se3–C6	110.1(3)
Se1–Pt–Se2	94.17(3)	Pt–Se3–C17	106.1(2)
Se2–Pt–Se3	97.40(3)	Se1–C7–Fe1	123.6(4)
Pt–Se1–C1	106.7(3)	Se3–C17–Fe2	126.2(4)

Torsion angles [°]			
Cl–Pt–Se1–C7	112.6(3)	Se1–Pt–Se2–C3	–44.0(3)
Cl–Pt–Se3–C17	–100.9(3)	Se3–Pt–Se2–C4	31.6(4)
Cl–Pt–Se1–C1	–142.8(3)	Se2–Pt–Se1–C7	–60.6(2)
Cl–Pt–Se3–C6	156.6(4)	Se2–Pt–Se3–C17	72.5(2)
Cl–Pt–Se2–C3	–117.7(6)	C1–Se1–C7–C8	–111.3(8)
Cl–Pt–Se2–C4	141.9(7)	C6–Se3–C17–C21	106.7(8)

In the cation, the tridentate ligand adopts the *meso* conformation. The coordination geometry around Pt is substantially square planar, and the chlorine atom deviates the most [0.278(3) Å] from the plane through the metal and donor atoms. The values of the angles to the metal [Cl–Pt–Se2 172.96(7)°, Se1–Pt–Se3 167.77(3)°, Se1–Pt–Se2 94.17(3)° and Se2–Pt–Se3 97.40(3)°] show that the adjacent six-membered chelate rings in this structure do not match the square-planar geometry as well as the single ring of the diselenoether complex [Pt{FcSe(CH$_2$)$_3$SeFc}$_2$]$^{2+}$.[10] The chelate rings are in the puckered conformation, and the carbon atoms are slightly offset from the coordination plane, on the opposite side of the ferrocenyl groups. The two cyclopentadienyl rings attached to the same iron atom are basically coplanar. The average of the Fe1–C(Cp) distances is 2.035(17) Å and that of the Fe2–C(Cp) distances is 2.026(17) Å.

The ferrocene sp^2 C–Se bond lengths [Se1–C7 1.901(8) Å, Se3–C17 1.903(9) Å] are a little longer than that in the free ligand [Se2–C4 1.896(5) Å], as are the sp^3 C–Se bond lengths [1.960(9) and 1.965(10) Å formed by the peripheral Se atoms in the complex, 1.955(4) Å in the free ligand; 1.959(10) and 1.971(9) Å formed by the central Se atom in the complex, 1.947(4) Å in the free ligand]. The Pt–Cl$_{trans\mathrm{Se}}$ bond length is 2.316(2) Å, which is shorter than those in [PtCl{MeS(CH$_2$)$_3$Te(CH$_2$)$_3$SMe}]PF$_6$ [Pt–Cl$_{trans\mathrm{Te}}$ 2.354(4) Å][8] and *cis*-[PtCl$_2$(EtOC$_6$H$_4$TeCH$_2$CH$_2$SMe)] [Pt–Cl$_{trans\mathrm{Te}}$ 2.336(3) Å];[14] this can be attributed to the weaker donor property of Se relative to that of Te. By contrast, the Pt–Se2 [2.3699(9) Å] bond is obviously shorter than the other two Pt–Se bonds [2.4126(9) and 2.4158(9) Å], and it is also out of the range of other Pt–Se bond lengths formed by *trans* Se pairs, such as the 2.4274(5) and 2.4386(7) Å distances found for [Pt{FcSe(CH$_2$)$_3$SeFc}$_2$](PF$_6$)$_2$·2MeCN,[10] the 2.414(2) and 2.421(2) Å distances in [Pt{MeSe(CH$_2$)$_3$SeMe}$_2$](PF$_6$)$_2$·2MeCN[15] and the 2.420(3) and 2.417(3) Å ones in [Pt({16}aneSe$_4$)](PF$_6$)$_2$·2MeCN.[16] This is good evidence that the *trans* influence of the Cl$^-$ anion is smaller than that of SeR$_2$.

Electrochemistry

Cyclic voltammetry [CV; supplemented by differential pulse voltammetry (DPV) where appropriate] was used to investigate the electrochemistry of the complexes in acetonitrile solution, and the data obtained are summarised in Table 3. In complexes containing two ferrocenyl moieties this technique provides a measure of the effectiveness of the

Table 3. Cyclic voltammetric data $E_{1/2}$ ($|E_{pa} - E_{pc}|$) [mV][a] for $FcE(CH_2)_3E'(CH_2)_3EFc$ and complexes.

	$FcSe(CH_2)_3Se(CH_2)_3SeFc$	$FcSe(CH_2)_3Te(CH_2)_3SeFc$		$FcTe(CH_2)_3Se(CH_2)_3TeFc$		$FcTe(CH_2)_3Te(CH_2)_3TeFc$	
Free ligand L	43 (75)	60 (100)	254 (77)	43 (106)	332 (72)	66 (90)	281(63)
$[PdClL]PF_6$	399 (113)	291 (114)		275 (107)		252 (98)	
$[PtClL]PF_6$	335 (114)	305 (112)		246 (116)		256 (123)	

[a] $E_{1/2}$ values are quoted relative to $FcH/[FcH]^+$.

bridging groups in facilitating interaction between the iron centres.[17–20] When two ferrocenyl moieties interact electronically with each other, they do not undergo oxidation at the same potential, and the difference between the two can be used to evaluate the magnitude of the interaction.[19] In these and related systems, communication between the ferrocenyl groups is believed to occur by a "through-bond" mechanism rather than a "through-space" mechanism.[21]

In previous electrochemistry studies of $FcE(CH_2)_nEFc$,[9] $[M\{FcE(CH_2)_3E'Fc\}_2](PF_6)_2$ (M = Pd or Pt; E, E′ = Se or Te)[10] and $[M'(CO)_4\{FcE(CH_2)_3E'Fc\}]$ (M = Cr, Mo or W),[11] it was noted that only when the through-bond Fe···Fe distance was less than a certain minimum value (in the range 13.17–13.37 Å) could interaction between the ferrocenyl moieties be observed. The crystal structure data of $FcSe(CH_2)_3Se(CH_2)_3SeFc$ show the through-bond length between the iron atoms to be 21.782(56) Å, which should be too long for significant interaction. As expected, only one wave is observed in the cyclic voltammogram, where $E_{1/2}$ = 43 mV (with respect to $FcH/[FcH]^+$), which is quite similar to the halfwave potential for oxidation of $FcSe(CH_2)_3SeFc$. In the cyclic voltammogram of $FcSe(CH_2)_3Te(CH_2)_3SeFc$ there are two reversible waves at $E_{1/2}$ = 60 and 254 mV. From the results for $FcSe(CH_2)_3Se(CH_2)_3SeFc$ and $FcTe(CH_2)_nTeFc$, it can be concluded that only the first one is based on the ferrocene moieties, and the second one is based on tellurium.[22] The other tellurium-containing compounds, $FcTe(CH_2)_3E'(CH_2)_3TeFc$ (E′ = Se or Te), behave similarly, and the only significant difference is that the relative intensity of the tellurium-based redox process depends on the number of tellurium atoms in the compound.

The through-bond length between the iron atoms of $[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]PF_6$ may be calculated from the crystal structure data to be 12.66 Å. This distance is even smaller than that in $[Pt\{FcSe(CH_2)_3SeFc\}_2](PF_6)_2$ (12.71 Å), so on this basis stronger communication between the ferrocenyl moieties would be predicted. However, only one quasireversible ($|E_{pa} - E_{pc}|$ = 114 mV) wave is observed in the CV at $E_{1/2}$ = 335 mV (Figure 5), and the DPV does not show the expected two peaks. Similarly, the other three complexes of the type $[MCl\{FcSe(CH_2)_3E'(CH_2)_3SeFc\}]PF_6$ also exhibit only one quasireversible wave, shifted anodically with respect to the free ligand.

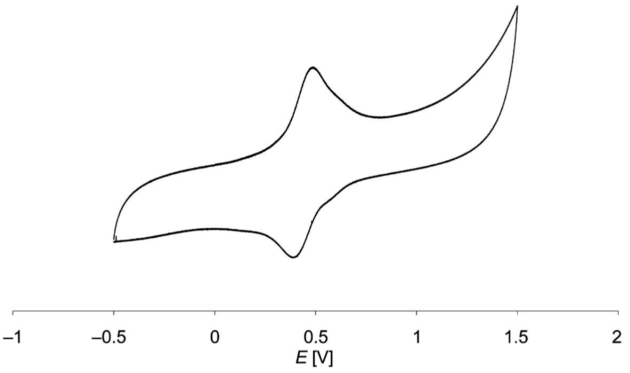


Figure 5. Cyclic voltammogram of $[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]PF_6$ in dry acetonitrile and 0.1 M tetrabutylammonium hexafluorophosphate at a scan rate of 100 mV s^{-1}.

This initially surprising result shows that in addition to the through-bond Fe···Fe distance and the nature of the intervening atoms (the "atomic pathway" for communication), there must be another factor involved in determining whether the intramolecular interaction between ferrocenes can be observed. Examination of the structural differences between $[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]PF_6$ and $[Pt\{FcSe(CH_2)_3SeFc\}_2](PF_6)_2$ (space-filling diagrams of the cations are shown in Figure 6) suggests that the symmetry is also important. Effectively, in these square-planar complexes transmission of the interaction through the group 10 metal atom only takes place when the ferrocenyl groups are substituents of *cis* donor atoms.

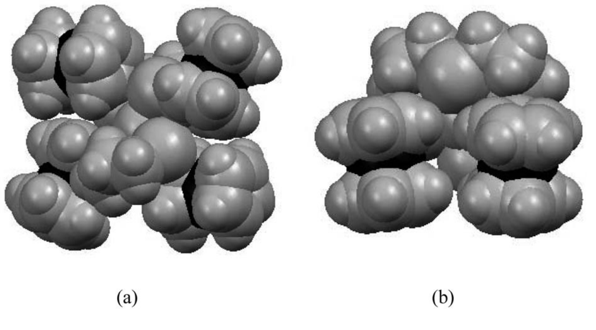

(a) (b)

Figure 6. Space-filling diagrams (Fe in black): (a) $[Pt\{FcSe(CH_2)_3SeFc\}_2]^{2+}$; (b) $[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]^+$.

In $[Pt\{FcSe(CH_2)_3SeFc\}_2](PF_6)_2$, there are four ferrocenyl moieties. The Pt atom is on an inversion centre, which means the two *trans* ferrocenyl moieties are structurally equivalent, so they will be oxidised at the same potential; in the CV this leads to the first oxidation wave. The second wave in the CV corresponds to oxidation (at a higher potential) of the two *cis* ferrocene units. In $[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]PF_6$, there are two ferrocenyl moieties in *trans* positions, which are symmetry related. The ^{77}Se NMR spectrum of $[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]PF_6$ shows that the *meso* invertomer observed in the solid state is the main form in solution. The *trans* ferrocenyl moieties are thus structurally equivalent and will be oxidised at the same potential. There are, of course, no *cis* ferrocene units, so no second wave is observed.

Although no crystal structures were obtained for the four complexes of the ferrocenyl telluride ligands FcTe$(CH_2)_3$-E′$(CH_2)_3$TeFc, by extrapolation of information relating to the bidentate ligand FcTe$(CH_2)_3$TeFc, we can predict that the through-bond length between the Fe···Fe centres is too long for communication. So regardless of the molecular symmetry, in these cases the ferrocene units can have no interaction.

All the complexes display an irreversible reduction process in the range from –0.85 to –1.45 V, which is attributed to the M^{II}/M^0 couple.[23]

Experimental Section

Materials and General Procedures: All the reactions below were carried out under an atmosphere of nitrogen by using standard Schlenk techniques. All solvents were distilled from elemental alkali metal or Na/K alloy, except ethanol (which was degassed before use), acetonitrile and dichloromethane (which was distilled from calcium hydride). Fc_2E_2 (E = Se, Te) were prepared from [Fe(η^5-$C_5H_5)_2$] (FcH) by lithiation in thf with Li*t*Bu (0.9 equiv.), treatment with selenium or tellurium and air oxidation in a minor modification of a literature procedure.[24,25]

Physical Measurements: ^1H and ^{13}C NMR spectra: Bruker AC400 (400 and 100 MHz, respectively); tetramethylsilane as internal standard. ^{77}Se and ^{125}Te NMR spectra: Bruker WM250 (47.7 and 78.9 MHz, respectively); dimethyl selenide or dimethyl telluride as external standard. IR spectra: Perkin–Elmer Spectrum One FTIR Spectrometer. UV/Vis spectra: UNICAM UV 300 UV/Vis Spectrometer in 1-cm quartz cells at room temperature. Elemental analyses were performed by the Warwick Analytical Service, University of Warwick Science Park, Coventry, UK. Mass spectra were recorded by the EPSRC Mass Spectrometry Centre by using electron impact (EI), fast atom bombardment (FAB), matrix-assisted laser desorption ionisation (MALDI) or positive ion electrospray (ES). Data are given as *m*/*z* values and are rounded to the nearest integer or half integer. Assignments are based on isotopomers containing ^1H, ^{12}C, ^{35}Cl, ^{56}Fe, ^{79}Br, ^{80}Se, ^{130}Te and ^{106}Pd or ^{195}Pt; expected isotope distribution patterns were observed. Cyclic voltammetry and differential pulse voltammetry measurements were performed at room temperature in a dry acetonitrile solution containing 0.1 M $[NBu_4]PF_6$ electrolyte by using an Autolab PGSTAT30 potentiostat system. The sweep rate was 100 mV s^{-1} (CV) or 72 mV s^{-1} (DPV). A three-electrode arrangement was used with a Pt working electrode, a Pt wire counter electrode and a Ag/Ag$^+$ (0.01 M $AgNO_3$ in CH_3CN) reference electrode. $E_{1/2}$ (CV) and E_p (DPV) values are quoted with respect to FcH/[FcH]$^+$. In the case of $E_{1/2}$ the value of $|E_{pa} - E_{pc}|$ is given in brackets. The halfwave potential of the FcH/[FcH]$^+$ redox couple under these conditions was 72 (80) mV.

Syntheses of FcE$(CH_2)_3$Br (E = Se or Te): The same general procedure was used for the syntheses of FcE$(CH_2)_3$Br (E = Se or Te), which is illustrated below by the example of FcSe$(CH_2)_3$Br.

Fc_2Se_2 (0.527 g, 1 mmol) was dissolved in EtOH (50 mL), and the solution was cooled to 0 °C. $NaBH_4$ (0.151 g, 4 mmol) was then added. After warming to room temperature and stirring for 2 h, the mixture became homogeneous. Then at 0 °C, this solution was slowly transferred to a dilute ethanol solution (200 mL) containing an excess amount of 1,3-dibromopropane. The reaction was allowed to continue for 2 h at 0 °C, with the solution colour changing to yellow. The solvent was removed by evaporation under reduced pressure. The residue was treated with water (25 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The extract was dried with $MgSO_4$, and the solvents evaporated to dryness. The residue was then subjected to column chromatography on SiO_2 (hexane/dichloromethane, 3:1) to give the product FcSe$(CH_2)_3$Br, which was generally isolated as an orange oil in excellent yield.

FcSe$(CH_2)_3$Br: Yield: 90%. ^1H NMR ($CDCl_3$): δ = 4.23 (m, 2 H, C_5H_4, 2,5-H), 4.13 (m, 2 H, C_5H_4, 3,4-H), 4.12 (s, 5 H, C_5H_5), 3.40 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, CH_2Br), 2.61 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H, SeCH_2), 2.01 (m, 2 H, $CH_2CH_2CH_2$) ppm. ^{13}C NMR ($CDCl_3$): δ = 75.8 (C_5H_4, C-2,5), not observed (C_5H_4, C-1), 70.3 (C_5H_4, C-3,4), 69.8 (C_5H_5), 33.6 (CH_2Br), 33.4 ($CH_2CH_2CH_2$), 27.8 ($^1J_{Se,C}$ = 63.3 Hz, SeCH_2) ppm. ^{77}Se NMR ($CDCl_3$): δ = 186 ppm. MS (EI): *m*/*z* (%) = 386 (45) [M]$^+$, 265 (100) [FcSe]$^+$.

FcTe$(CH_2)_3$Br: Yield: 80%. ^1H NMR ($CDCl_3$): δ = 4.28 (m, 2 H, C_5H_4, 2-H, 5-H), 4.16 (m, 2 H, C_5H_4, 3-H, 4-H), 4.09 (s, 5 H, C_5H_5), 2.35 (t, $^3J_{H,H}$ = 8.3 Hz, 2 H, CH_2Br), 2.59 (t, $^3J_{H,H}$ = 6.3 Hz, 2 H, TeCH_2), 2.12 (m, 2 H, $CH_2CH_2CH_2$) ppm. ^{13}C NMR ($CDCl_3$): δ = 79.9 (C_5H_4, C-2,5), 71.8 (C_5H_4, C-3,4), 69.7 (C_5H_5), 43.1 (C_5H_4, C-1), 35.7 (CH_2Br), 35.1 ($CH_2CH_2CH_2$), 6.5 (FcTeCH_2) ppm. ^{125}Te NMR ($CDCl_3$): δ = 299 ppm. MS (EI): *m*/*z* (%) = 436 (42) [M]$^+$, 315 (100) [FcTe]$^+$.

Syntheses of FcE$(CH_2)_3$E′$(CH_2)_3$EFc (E, E′ = Se or Te): The same general procedure was used for the syntheses of FcE$(CH_2)_3$E′$(CH_2)_3$-EFc (E, E′ = Se or Te), which is illustrated below by the example of FcSe$(CH_2)_3$Se$(CH_2)_3$SeFc.

Se (0.055 g, 0.7 mmol) and $NaBH_4$ (0.05 g, 1.4 mmol) were heated at reflux in degassed ethanol (50 mL) under N_2 for 1 h to produce a clear solution. A thf solution of FcSe$(CH_2)_3$Br (0.544 g, 1.4 mmol) was then added slowly, and the mixture was left to stir for 12 h. After removing the solvent by evaporation under reduced pressure, the residue was treated with water (25 mL) and then extracted with CH_2Cl_2 (3 × 25 mL). The extract was dried with $MgSO_4$, and the solvents evaporated to dryness. The residue was then subjected to column chromatography on SiO_2 (hexane/dichloromethane, 3:1) to produce four bands. The fourth band contained FcSe$(CH_2)_3$Se$(CH_2)_3$SeFc, a yellow powder with yield 0.269 g (56%).

FcSe$(CH_2)_3$Se$(CH_2)_3$SeFc: Yield: 56%. ^1H NMR ($CDCl_3$): δ = 4.24 (m, 4 H, C_5H_4, 2,5-H), 4.13 (m, 4 H, C_5H_4, 3,4-H), 4.12 (s, 10 H, C_5H_5), 2.56 (t, 4 H, FcSeCH_2), 2.48 (t, 4 H, CH_2SeCH_2), 1.82 (m, 4 H, $CH_2CH_2CH_2$) ppm. ^{13}C NMR ($CDCl_3$): δ = 75.7 (C_5H_4, C-2,5), 70.9 (C_5H_4, C-1), 70.2 (C_5H_4, C-3,4), 69.9 (C_5H_5), 31.4 ($CH_2CH_2CH_2$), 29.7 (FcSeCH_2), 23.8 ($^1J_{C,Se}$ = 62 Hz, CH_2SeCH_2) ppm. ^{77}Se NMR ($CDCl_3$): δ = 190 (FcSe), 154 (CH_2SeCH_2) ppm. MS (FAB): *m*/*z* (%) = 692 (53) [M]$^+$, 265 (100) [FcSe]$^+$. $C_{26}H_{30}Fe_2Se_3$ (691.10): calcd. C 45.2, H 4.38; found C 44.1, H 4.30.

FcSe$(CH_2)_3$Te$(CH_2)_3$SeFc: Yield: 50%. ^1H NMR ($CDCl_3$): δ = 4.23 (m, 4 H, C_5H_4, 2,5-H), 4.13 (m, 4 H, C_5H_4, 3,4-H), 4.12 (s, 10 H, C_5H_5), 2.54 (m, 8 H, SeCH_2, CH_2Te), 1.89 (m, 4 H, $CH_2CH_2CH_2$) ppm. ^{13}C NMR ($CDCl_3$): δ = 75.7 (C_5H_4, C-2,5), 70.6 (C_5H_4, C-1), 70.0 (C_5H_4, C-3,4), 69.8 (C_5H_5), 32.9 ($CH_2CH_2CH_2$), 31.8 (SeCH_2), 2.7 ($^1J_{C,Te}$ = 156 Hz, CH_2Te) ppm. ^{77}Se NMR ($CDCl_3$): δ = 189 ppm. ^{125}Te NMR ($CDCl_3$): δ = 228 ppm. MS (FAB): *m*/*z* (%) = 738 (6) [M]$^+$, 265 (100) [FcSe]$^+$. $C_{26}H_{30}Fe_2Se_2Te$ (739.74): calcd. C 42.2, H 4.09; found C 40.9, H 3.91.

FcTe(CH$_2$)$_3$Se(CH$_2$)$_3$TeFc: Yield: 40%. ^{1}H NMR (CDCl$_3$): δ = 4.28 (m, 4 H, C$_5$H$_4$, 2,5-H), 4.14 (m, 4 H, C$_5$H$_4$, 3,4-H), 4.09 (s, 10 H, C$_5$H$_5$), 2.57 (t, 4 H, TeCH$_2$), 2.45 (t, 4 H, CH$_2$Se), 1.91 (m, 4 H, CH$_2$CH_2CH$_2$) ppm. ^{13}C NMR (CDCl$_3$): δ = 78.3 (C$_5$H$_4$, C-2,5), 70.2 (C$_5$H$_4$, C-3,4), 68.2 (C$_5$H$_5$), 42.3 ($^1J_{\text{C,Te}}$ = 304 Hz, C$_5$H$_4$, C-1), 31.3 (CH$_2$CH$_2$CH$_2$), 24.6 ($^1J_{\text{C,Se}}$ = 63 Hz, CH$_2$Se), 7.4 ($^1J_{\text{C,Te}}$ = 158 Hz, TeCH$_2$) ppm. ^{77}Se NMR (CDCl$_3$): δ = 151 ppm. ^{125}Te NMR (CDCl$_3$): δ = 301 ppm. MS (FAB): m/z (%) = 790 (25) [M]$^+$, 315 (100) [FcTe]$^+$. C$_{26}$H$_{30}$Fe$_2$SeTe$_2$ (788.38): calcd. C 39.6, H 3.84; found C 39.1, H 3.73.

FcTe(CH$_2$)$_3$Te(CH$_2$)$_3$TeFc: Yield: 48%. ^{1}H NMR (CDCl$_3$): δ = 4.28 (m, 4 H, C$_5$H$_4$, 2,5-H), 4.15 (m, 4 H, C$_5$H$_4$, 3,4-H), 4.09 (s, 10 H, C$_5$H$_5$), 2.53 (m, 8 H, FcTeCH$_2$, CH$_2$TeCH$_2$), 1.97 (m, 4 H, CH$_2$CH_2CH$_2$) ppm. ^{13}C NMR (CDCl$_3$): δ = 79.8 (C$_5$H$_4$, C-2,5), 71.7 (C$_5$H$_4$, C-3,4), 69.7 (C$_5$H$_5$), 43.8 ($^1J_{\text{C,Te}}$ = 306 Hz, C$_5$H$_4$, C-1), 34.3 (CH$_2$CH$_2$CH$_2$), 11.3 ($^1J_{\text{C,Te}}$ = 158 Hz, FcTeCH$_2$), 5.4 ($^1J_{\text{C,Te}}$ = 156 Hz, CH$_2$TeCH$_2$) ppm. ^{125}Te NMR (CDCl$_3$): δ = 299 ($^4J_{\text{Te,Te}}$ = 43 Hz, FcTe), 233 ($^4J_{\text{Te,Te}}$ = 43 Hz, CH$_2$TeCH$_2$) ppm. MS (FAB): m/z (%) = 838 (8) [M]$^+$, 315 (58) [FcTe]$^+$. C$_{26}$H$_{30}$Fe$_2$Te$_3$ (837.02): calcd. C 37.3, H 3.61; found C 38.6, H 3.62.

Syntheses of [MCl{FcE(CH$_2$)$_3$E′(CH$_2$)$_3$EFc}]PF$_6$ (M = Pd or Pt; E, E′ = Se or Te): The same general procedure was used for the syntheses of these eight complexes, which is illustrated below by the example of [PtCl{FcSe(CH$_2$)$_3$Se(CH$_2$)$_3$SeFc}]PF$_6$.

PtCl$_2$ (96 mg, 0.36 mmol) was heated at reflux in MeCN (30 mL) for 2 h to give a yellow solution of [PtCl$_2$(NCMe)$_2$]. TlPF$_6$ (102 mg, 0.18 mol) was added and reflux was continued for another 15 min. FcSe(CH$_2$)$_3$Se(CH$_2$)$_3$SeFc (250 mg, 0.36 mmol) in CH$_2$Cl$_2$ (5 mL) was then added dropwise. The mixture was stirred at room temperature for 24 h to give a peach red liquid and a fine white precipitate of TlCl. The solution was centrifuged to remove TlCl and reduced to 2 mL in vacuo; diethyl ether (10 mL) was added to precipitate an orange-red powder.

[PdCl{FcSe(CH$_2$)$_3$Se(CH$_2$)$_3$SeFc}]PF$_6$: Blue powder. Yield: 70%. ^{1}H NMR (CD$_3$COCD$_3$, major invertomer only): δ = 4.79 (m, 2 H, C$_5$H$_4$, 2-H), 4.67 (m, 2 H, C$_5$H$_4$, 5-H), 4.48 (m, 2 H, C$_5$H$_4$, 3-H), 4.46 (m, 2 H, C$_5$H$_4$, 4-H), 4.37 (s, 10 H, C$_5$H$_5$), 3.20 (m, 2 H, FcSeCH$_2$), 3.05 (m, 6 H, FcSeCH$_2$, CH$_2$SeCH$_2$), 2.48 (m, 2 H, CH$_2$CH_2CH$_2$), 2.04 (m, 2 H, CH$_2$CH_2CH$_2$) ppm. ^{13}C NMR (CDCl$_3$, major invertomer only): δ = 75.3 (C$_5$H$_4$, C-2,5), 72.6 (C$_5$H$_4$, C-3,4), 72.2 (C$_5$H$_4$, C-1), 71.9 (C$_5$H$_5$), 33.5 (CH$_2$CH_2CH$_2$), 31.1 (FcSeCH$_2$), 26.4 (CH$_2$SeCH$_2$) ppm. ^{77}Se NMR (CD$_3$COCD$_3$): δ = 227 (FcSe), 202 (CH$_2$SeCH$_2$) ppm. MS (ES): m/z = 835 [M – PF$_6$]$^+$. C$_{26}$H$_{30}$ClF$_6$Fe$_2$PPdSe$_3$ (977.91): calcd. C 31.9, H 3.09; found C 31.2, H 3.03.

[PtCl{FcSe(CH$_2$)$_3$Se(CH$_2$)$_3$SeFc}]PF$_6$: Orange-red powder. Yield: 60%. ^{1}H NMR (CD$_3$CN, major invertomer only): δ = 4.99 (m, 2 H, C$_5$H$_4$, 2-H), 4.83 (m, 2 H, C$_5$H$_4$, 5-H), 4.64 (m, 4 H, C$_5$H$_4$, 3,4-H), 4.53 (s, 10 H, C$_5$H$_5$), 3.46 (m, 2 H, FcSeCH$_2$), 3.27 (m, 2 H, FcSeCH$_2$), 3.23 (m, 4 H, CH$_2$SeCH$_2$), 2.77 (m, 2 H, CH$_2$CH_2CH$_2$), 2.20 (m, 2 H, CH$_2$CH_2CH$_2$) ppm. ^{13}C NMR (CD$_3$CN, major invertomer only): δ = 74.6 (C$_5$H$_4$, C-2), 72.5 (C$_5$H$_4$, C-5), 72.0 (C$_5$H$_4$, C-3), 71.8 (C$_5$H$_5$), 71.7 (C$_5$H$_4$, C-4), not observed (C$_5$H$_4$, C-1), 34.2 (CH$_2$CH_2CH$_2$), 30.8 (FcSeCH$_2$), 26.6 (CH$_2$SeCH$_2$) ppm. ^{77}Se NMR (CD$_3$COCD$_3$): δ = 220 ($^1J_{\text{Pt,Se}}$ = 388 Hz, FcSe), 200 ($^1J_{\text{Pt,Se}}$ = 268 Hz, CH$_2$SeCH$_2$) ppm. MS (ES): m/z = 924 [M – PF$_6$]$^+$. C$_{26}$H$_{30}$ClF$_6$Fe$_2$PPtSe$_3$ (1066.60): calcd. C 29.3, H 2.84; found C 29.3, H 2.85.

[PdCl{FcSe(CH$_2$)$_3$Te(CH$_2$)$_3$SeFc}]PF$_6$: Blue powder. Yield: 60%. ^{1}H NMR (CD$_3$CN, major invertomer only): δ = 4.70 (s, 2H C$_5$H$_4$, 2-H), 4.64 (s, 2 H, C$_5$H$_4$, 5-H), 4.54 (s, 4 H, C$_5$H$_4$, 3,4-H), 4.47 (s, 10 H, C$_5$H$_5$), 3.18 (m, 2H FcSeCH$_2$), 2.96 (m, 4 H, CH$_2$TeCH$_2$), 2.78 (m, 2 H, FcSeCH$_2$), 2.26 (m, 2 H, CH$_2$CH_2CH$_2$), 2.13 (m, 2 H, CH$_2$CH_2CH$_2$) ppm. ^{13}C NMR (CD$_3$CN, major invertomer only): δ = 73.8 (C$_5$H$_4$, C-2,5), 71.0 (C$_5$H$_4$, C-3,4), 70.3 (C$_5$H$_5$), not observed (C$_5$H$_4$, C-1), 33.1 (CH$_2$CH_2CH$_2$), 25.8 (FcSeCH$_2$), 13.0 (CH$_2$Te) ppm. ^{77}Se NMR (CDCl$_3$): δ = 195 ppm. ^{125}Te NMR (CDCl$_3$): not resolved. MS (FAB): m/z = 885 [M – PF$_6$]$^+$. C$_{26}$H$_{30}$ClF$_6$Fe$_2$PPdSe$_2$Te (1026.55): calcd. C 30.4, H 2.95; found C 26.1, H 2.52.

[PtCl{FcSe(CH$_2$)$_3$Te(CH$_2$)$_3$SeFc}]PF$_6$: Red powder. Yield: 85%. ^{1}H NMR (CD$_3$CN, major invertomer only): δ = 4.77 (m, 2 H, C$_5$H$_4$, 2-H), 4.66 (m, 2 H, C$_5$H$_4$, 5-H), 4.58 (m, 4 H, C$_5$H$_4$, 3,4-H), 4.49 (s, 10 H, C$_5$H$_5$), 3.26 (m, 2 H, FcSeCH$_2$), 2.97 (m, 4 H, CH$_2$TeCH$_2$), 2.78 (m, 2 H, FcSeCH$_2$), 2.34 (m, 2 H, CH$_2$CH_2CH$_2$), 2.04 (m, 2 H, CH$_2$CH_2CH$_2$) ppm. ^{13}C NMR (CD$_3$CN, major invertomer only): δ = 73.2 (C$_5$H$_4$, C-2), 71.3 (C$_5$H$_4$, C-5), 70.9 (C$_5$H$_4$, C-3), 70.2 (C$_5$H$_5$), 70.0 (C$_5$H$_4$, C-4), not observed (C$_5$H$_4$, C-1), 33.8 (CH$_2$CH_2CH$_2$), 25.8 (FcSeCH$_2$), 11.0 (CH$_2$Te) ppm. ^{77}Se NMR (CD$_3$CN): δ = 217 ($^1J_{\text{Pt,Se}}$ = 399 Hz) ppm. ^{125}Te NMR (CD$_3$CN): not resolved. MS (MALDI): m/z = 974 [M – PF$_6$]$^+$. C$_{26}$H$_{30}$ClF$_6$Fe$_2$PPtSe$_2$Te (1115.24): calcd. C 28.0, H 2.62; found C 25.2, H 2.47.

[PdCl{FcTe(CH$_2$)$_3$Se(CH$_2$)$_3$TeFc}]PF$_6$: Blue powder. Yield: 85%. ^{1}H NMR (CD$_3$CN, major invertomer only): δ = 4.73 (m, 2 H, C$_5$H$_4$, 2-H), 4.60 (m, 2 H, C$_5$H$_4$, 5-H), 4.56 (m, 4 H, C$_5$H$_4$, 3,4-H), 4.42 (s, 10 H, C$_5$H$_5$), 3.03–2.70 (m, 8 H, FcTeCH$_2$, CH$_2$SeCH$_2$), 2.20 (m, 2 H, CH$_2$CH_2CH$_2$), 2.04 (m, 2 H, CH$_2$CH_2CH$_2$) ppm. ^{13}C NMR (CD$_3$CN, major invertomer only): δ = 76.4 (C$_5$H$_4$, C-2), 74.1 (C$_5$H$_4$, C-5), 71.9 (C$_5$H$_4$, C-3), 71.7 (C$_5$H$_4$, C-4), 70.0 (C$_5$H$_5$), 48.2 (C$_5$H$_4$, C-1), 32.0 (CH$_2$CH_2CH$_2$), 25.5 (CH$_2$SeCH$_2$), 17.0 (FcTeCH$_2$) ppm. ^{77}Se NMR (CD$_3$CN): δ = 232 (minor), 226 (major) ppm. ^{125}Te (CD$_3$CN): not resolved. MS (ES): m/z = 935 [M – PF$_6$]$^+$. C$_{26}$H$_{30}$ClF$_6$Fe$_2$PPdSeTe$_2$ (1075.19): calcd. C 29.0, H 2.81; found C 24.7, H 2.36.

[PtCl{FcTe(CH$_2$)$_3$Se(CH$_2$)$_3$TeFc}]PF$_6$: Red powder. Yield: 85%. ^{1}H NMR (CD$_3$CN, major invertomer only): δ = 4.81 (m, 2 H, C$_5$H$_4$, 2-H), 4.59 (m, 4 H, C$_5$H$_4$, 3,4-H), 4.58 (m, 2 H, C$_5$H$_4$, 5-H), 4.43 (s, 10 H, C$_5$H$_5$), 3.07–2.83 (m, 8 H, FcTeCH$_2$, CH$_2$SeCH$_2$), 2.37 (m, 2 H, CH$_2$CH_2CH$_2$), 2.08 (m, 2 H, CH$_2$CH_2CH$_2$) ppm. ^{13}C NMR (CD$_3$CN, major invertomer only): δ = 75.8 (C$_5$H$_4$, C-2), 74.0 (C$_5$H$_4$, C-5), 72.2 (C$_5$H$_4$, C-3), 71.3 (C$_5$H$_4$, C-4), 69.9 (C$_5$H$_5$), 47.5 (C$_5$H$_4$, C-1), 31.8 (CH$_2$CH_2CH$_2$), 25.7 (CH$_2$SeCH$_2$), 16.9 (FcTeCH$_2$) ppm. ^{77}Se NMR (CD$_3$CN): δ = 204.4 (minor), 204.0 (major, $^1J_{\text{Pt,Se}}$ = 187 Hz) ppm. ^{125}Te (CD$_3$CN): δ = 357.0 (major, $^1J_{\text{Pt,Te}}$ = 480 Hz), 356.7 (minor) ppm. MS (ES): m/z = 1024 [M – PF$_6$]$^+$. C$_{26}$H$_{30}$ClF$_6$Fe$_2$PPtSeTe$_2$ (1163.88): calcd. C 26.8, H 2.60; found C 26.9, H 2.59.

[PdCl{FcTe(CH$_2$)$_3$Te(CH$_2$)$_3$TeFc}]PF$_6$: Dark blue powder. Yield: 80%. ^{1}H NMR (CD$_3$CN, major invertomer only): δ = 4.83–4.50 (m, 8 H, C$_5$H$_4$, 2,5-H, 3,4-H), 4.42 (s, 10 H, C$_5$H$_5$), 3.35–2.60 (m, 8 H, FcTeCH$_2$, CH$_2$TeCH$_2$), 2.30–2.05 (m, 4 H, CH$_2$CH_2CH$_2$) ppm. ^{13}C NMR (CD$_3$CN, major invertomer only): δ = 76.3 (C$_5$H$_4$, C-2), 74.1 (C$_5$H$_4$, C-5), 72.0 (C$_5$H$_4$, C-3), 71.7 (C$_5$H$_4$, C-4), 70.0 (C$_5$H$_5$), 40.6 (C$_5$H$_4$, C-1), 27.0 (CH$_2$CH_2CH$_2$), 17.9 (FcTeCH$_2$), 14.7 (CH$_2$TeCH$_2$) ppm. ^{125}Te NMR (CDCl$_3$): not resolved. MS (ES): m/z = 985 [M – PF$_6$]$^+$. C$_{26}$H$_{30}$ClF$_6$Fe$_2$PPdTe$_3$ (1123.83): calcd. C 27.8, H 2.69; found C 24.2, H 2.35.

[PtCl{FcTe(CH$_2$)$_3$Te(CH$_2$)$_3$TeFc}]PF$_6$: Dark red powder. Yield: 90%. ^{1}H NMR (CD$_3$CN, major invertomer only): δ = 4.93–4.63 (m, 8 H, C$_5$H$_4$, 2,5-H, 3,4-H), 4.53 (s, 10 H, C$_5$H$_5$), 3.45–2.80 (m, 8 H, FcTeCH$_2$, CH$_2$TeCH$_2$), 2.30–2.00 (m, 4 H, CH$_2$CH_2CH$_2$) ppm. ^{13}C NMR (CD$_3$CN, major invertomer only): δ = 75.9 (C$_5$H$_4$, C-2), 74.1 (C$_5$H$_4$, C-5), 72.3 (C$_5$H$_4$, C-3), 71.3 (C$_5$H$_4$, C-4), 69.9

Table 4. Crystal data and structure refinement for $FcSe(CH_2)_3Se(CH_2)_3SeFc$ and $[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]PF_6$.

	$FcSe(CH_2)_3Se(CH_2)_3SeFc$	$[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]PF_6$
Empirical formula	$C_{26}H_{30}Fe_2Se_3$	$C_{26}H_{30}ClF_6Fe_2PPtSe_3$
Formula weight	691.08	1066.59
T [K]	296(2)	293(2)
Wavelength [Å]	0.71069	0.71069
Crystal system	orthorhombic	monoclinic
Space group	$F2dd$	$P2_1/n$
a [Å]	12.562(1)	20.049(2)
b [Å]	17.311(1)	7.631(1)
c [Å]	23.029(1)	20.181(2)
α [°]	90	90
β [°]	90	97.54(1)
γ [°]	90	90
Volume [Å^3]	5007.9(5)	3060.9(6)
Z	8	4
$D_{calcd.}$ [Mg m^{-3}]	1.833	2.315
Absorption coefficient [mm^{-1}]	5.532	9.255
$F(000)$	2720	2016
Crystal size [mm]	$0.40 \times 0.30 \times 0.20$	$0.40 \times 0.30 \times 0.08$
θ range for data collection [°]	4.38 to 26.37	4.06 to 26.37
Index ranges	$-15 \le h \le 15$, $-21 \le k \le 20$, $-28 \le l \le 28$	$-24 \le h \le 25$, $-9 \le k \le 9$, $-25 \le l \le 25$
Reflections collected	10461	41961
Independent reflections [$I > 2\sigma(I)$]	2546 [2214]	6203 [5182]
Data/restraints/parameters	2546/1/141	6203/18/362
Goodness-of-fit on F^2	1.009	1.124
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0324$, $wR_2 = 0.0744$	$R_1 = 0.0480$, $wR_2 = 0.1045$
R indices (all data)	$R_1 = 0.0390$, $wR_2 = 0.0771$	$R_1 = 0.0603$, $wR_2 = 0.1142$
Largest diff. peak, hole [e Å^{-3}]	0.466, –0.540	1.606, –1.467

(C_5H_5), 47.1 (C_5H_4, C-1), 27.0 ($CH_2CH_2CH_2$), 18.0 ($FcTeCH_2$), 13.3 (CH_2TeCH_2) ppm. ^{125}Te (CD_3CN): $\delta = 369$ (minor, FcTe), 355 (major, $^1J_{Pt,Te} = 515$ Hz, FcTe), 354 (major, $^1J_{Pt,Te} = 232$ Hz, CH_2TeCH_2) ppm. MS (FAB): $m/z = 1074$ $[M - PF_6]^+$. $C_{26}H_{30}ClF_6Fe_2PPtTe_3$ (1212.52): calcd. C 25.8, H 2.49; found C 25.3, H 2.51.

X-ray Crystallography: Crystals of $FcSe(CH_2)_3Se(CH_2)_3SeFc$ were obtained from CH_2Cl_2/hexanes. Crystals of $[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]PF_6$ were grown by vapour diffusion of diethyl ether into a solution of the complex in acetone. Data collections were performed at room temperature with an Oxford Diffraction Xcalibur 3 CCD diffractometer and graphite-monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å). Intensity data sets were corrected for absorption analytically[26] for $FcSe(CH_2)_3Se(CH_2)_3SeFc$ and by a multiscan procedure for $[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]PF_6$.[27] The structures were solved by direct methods, that of the ligand by using SHELXS-97[28] and that of the Pt complex with SIR-97;[29] they were refined anisotropically for all non-hydrogen atoms with SHELXL-97.[30] Hydrogen atoms were in geometrically generated positions, riding, with the constraint $U_H = 1.2\ U_C^{eq}$ on thermal parameters. The absolute structure was assigned on the basis of Flack's test[31] [0.008(14) parameter value] in the case of $FcSe(CH_2)_3Se(CH_2)_3SeFc$, which crystallises in an acentric space group. For graphics ORTEP-3 was employed.[32] Crystal data, data collection parameters and analysis statistics of $FcSe(CH_2)_3Se(CH_2)_3SeFc$ and $[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]PF_6$ are summarised in Table 4; selected bond angles and distances of $FcSe(CH_2)_3Se(CH_2)_3SeFc$ and $[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]PF_6$ are listed in Tables 1 and 2, respectively. CCDC-682955 [for $FcSe(CH_2)_3Se(CH_2)_3SeFc$] and -682954 (for $[PtCl\{FcSe(CH_2)_3Se(CH_2)_3SeFc\}]PF_6$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] L. F. Szczepura, L. M. Witham, K. J. Takeuchi, *Coord. Chem. Rev.* **1998**, *174*, 5–32.

[2] R. S. Ali, J. Higgins, W. Levason, *Inorg. Chim. Acta* **1984**, *84*, 65–69.

[3] E. W. Abel, K. Kite, P. S. Perkins, *Polyhedron* **1986**, *5*, 1459–1465.

[4] D. J. Gulliver, E. G. Hope, W. Levason, S. G. Murray, D. M. Potter, G. L. Marshall, *J. Chem. Soc. Perkin Trans. 2* **1984**, 429–434.

[5] S. J. Loeb, J. R. Mansfield, *Can. J. Chem.* **1996**, *74*, 1377–1390.

[6] A. J. Barton, W. Levason, G. Reid, A. J. Ward, *Organometallics* **2001**, *20*, 3644–3649.

[7] M. Misra, A. K. Singh, *Phosphorus, Sulfur, Silicon, Relat. Elem.* **1998**, *134–135*, 537–543.

[8] M. Hesford, W. Levason, S. D. Orchard, G. Reid, *J. Organomet. Chem.* **2002**, *649*, 214–218.

[9] M. R. Burgess, S. Jing, C. P. Morley, *J. Organomet. Chem.* **2006**, *691*, 3484–3489.

[10] S. Jing, C. P. Morley, C. A. Webster, M. Di Vaira, *Dalton Trans.* **2006**, 4335–4342.

[11] S. Jing, C. P. Morley, C. A. Webster, M. Di Vaira, *J. Organomet. Chem.* **2008**, *693*, 2310–2316.

[12] E. G. Hope, W. Levason, S. G. Murray, G. L. Marshall, *J. Chem. Soc., Dalton Trans.* **1995**, 2185–2190.

[13] S. Hartmann, R. F. Winter, T. Scheiring, M. Wanner, *J. Organomet. Chem.* **2001**, *637–639*, 240–250.

[14] A. K. Singh, V. Srivastava, S. K. Dhingra, J. E. Drake, J. H. E. Bailey, *Acta Crystallogr., Sect. C* **1992**, *48*, 655–657.

[15] N. R. Champness, W. Levason, J. J. Quirk, G. Reid, C. S. Frampton, A. M. Z. Slawin, D. J. Williams, *Polyhedron* **1995**, *14*, 2753–2758.

[16] N. R. Champness, P. F. Kelly, W. Levason, G. Reid, A. M. Z. Slawin, D. J. Williams, *Inorg. Chem.* **1995**, *34*, 651–657.

[17] O. B. Sutcliffe, M. R. Bryce, A. S. Batsanov, *J. Organomet. Chem.* **2002**, *656*, 211–216.

[18] P. D. Beer, D. K. Smith, *J. Chem. Soc., Dalton Trans.* **1998**, 417–424.

[19] Y. Yamada, J. Mizutani, M. Kurihara, H. Nishihara, *J. Organomet. Chem.* **2001**, *637–639*, 80–83.

[20] J. M. Lloris, R. Martínez-Máñez, J. Soto, T. Pardo, *J. Organomet. Chem.* **2001**, *637–639*, 151–158.

[21] D. Osella, L. Milone, C. Nervi, M. Ravera, *J. Organomet. Chem.* **1995**, *488*, 1–7.

[22] M. R. Burgess, C. P. Morley, *J. Organomet. Chem.* **2001**, *623*, 101–108.

[23] V. C. Gibson, N. J. Long, C. K. Williams, M. Fontani, P. Zanello, *Dalton Trans.* **2003**, 3599–3605.

[24] M. Herberhold, P. Leitner, *J. Organomet. Chem.* **1987**, *336*, 153–161.

[25] G. Mugesh, A. Panda, H. B. Singh, N. S. Punekar, R. J. Butcher, *J. Am. Chem. Soc.* **2001**, *123*, 839–850.

[26] Oxford Diffraction, *CrysAlis RED* (version 1.171), Oxford Diffraction, Abingdon, Oxfordshire, England.

[27] G. M. Sheldrick, *SADABS: Program for Empirical Absorption Corrections*, University of Göttingen, **1986**.

[28] G. M. Sheldrick, *SHELXS-97: Program for Crystal Structure Solution*, University of Göttingen, **1997**.

[29] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. G. Iacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[30] G. M. Sheldrick, *SHELXL-97: Program for Crystal Structure Refinement*, University of Göttingen, **1997**.

[31] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876–881.

[32] a) C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN; b) L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565–566.

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