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(2,2-Dibromovinyl)ferrocene as a Building Block for the Assembly of Heterodinuclear Complexes – Preparation of an σ-Alkenylpalladium Complex and Dimetallic Dithioether Complexes

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The oxidative addition of (2,2-dibromovinyl)ferrocene [Br_2C=C(H)–Fc] (**1**) to [$Pd(PPh_3)_4$] yields the heterodinuclear σ-alkenyl complex *trans*-[{Pd(Br)$(PPh_3)_2$}–C(Br)=C(H)–Fc] (**2**). Nucleophilic attack of sodium thiolates on **1** unexpectedly affords the vinyl thioether derivatives (Z)-[(RS)(H)C=C(H)–Fc] (**4a**: R = Ph; **4b**: R = *t*Bu; **4c**: R = Et). Complexes **4a** and **4c** can also be prepared by addition of NaSR across the triple bond of Fc–C≡C–H (**3**). Addition of an excess of NaSR to **1** affords the dithioether derivatives (Z)-[(RS)(H)C=C(SR)–Fc] (**5a**: R = Ph; **5b**: R = *p*-tolyl; **5c**: R = Et). An addition/elimination sequence is suggested to account for this surprising result. The yield of **5c** is very low due to a competing formation of ethynylferrocene (**3**). Reaction of **5b** with [Re(thf)$(CO)_3$(μ-Br)]$_2$ and [$PtCl_2(PhCN)_2$] leads to the heterodinuclear chelate complexes [Fc{C(S–*p*-tolyl)=C(H)(S–*p*-tolyl)}Re(Br)$(CO)_3$] (**6**) and [Fc{C(S–*p*-tolyl)=C(H)(S–*p*-tolyl)}$PtCl_2$] (**7a**), respectively. Metathesis of the fluxional compound **7a** in the presence of NaI affords [Fc{C(S–*p*-tolyl)=C(H)(S–*p*-tolyl)}PtI_2] (**7b**). The electrochemical properties of some of these complexes have been studied by means of cyclic voltammetry, and the molecular structures of **1**, **2**, **3**, **4b**, **4c** and **6** have been determined by X-ray diffraction.
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Introduction

Ethynylferrocene[1] is increasingly being used as building block for the construction of di- and polymetallic organometallic systems[2–5] due to the presence of an electrochemically active ferrocenyl unit. In contrast, only a few examples of the preparation of polymetallic arrays starting from alkenylferrocenes have been reported in the literature.[6–9] In addition to a covalent connection to other metal centres, vinylferrocene has also been used as side-on bound π-ligand for the synthesis of dimetallic compounds of the type [$M(CO)_5\{\eta^2$-H_2C=C(H)Fc}] (M = Cr, Mo, W).[10] For the past few years, we have been interested in the assembly of homo- and heterodinuclear transition metal complexes and the evaluation of their physicochemical properties (electrochemistry, luminescence).[11] Indeed, we recently published the synthesis of (dibromovinyl)[2.2]paracyclophane and investigated its reactivity towards [$M(PPh_3)_4$] (M = Pd, Pt).[11c] For comparison, we embarked on a study on the reactivity of (2,2-dibromovinyl)ferrocene (**1**), which shares some common features with (dibromovinyl)[2.2]paracyclophane such as planar chirality, redox activity and potential applications in materials science. We now wish to report the use of **1** for the synthesis of a functionalised vinylpalladium(II) complex, the reactivity of **1** towards various thiolates (NaSR) and the subsequent rearrangement reactions that lead to vinylic thioether compounds, which may also serve as ligands in coordination chemistry. This work also includes electrochemical investigations and several crystal structure determinations.

Results and Discussion

Oxidative Addition of (2,2-Dibromovinyl)ferrocene (1) to [$Pd(PPh_3)_4$]

The starting material **1** was prepared according to a literature procedure under Corey–Fuchs conditions by treatment of ferrocenecarbaldehyde with CBr_4 in the presence of zinc dust and PPh_3 (Scheme 1).[12,13] An X-ray diffraction study (Figure 1) revealed that, in contrast to (dibromovinyl)[2.2]paracyclophane,[11c] the alkenyl unit and the cyclopentadienido ring are almost parallel, with an interplanar angle of only 10.43°.

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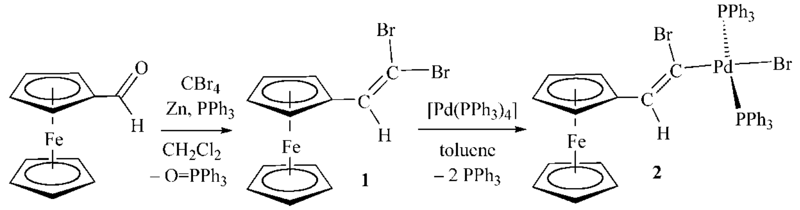


Scheme 1.

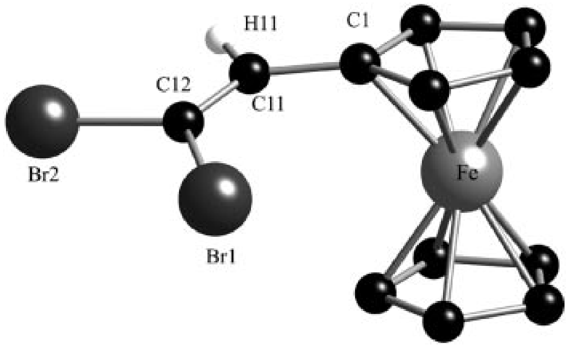


Figure 1. Ball-and-stick view of the molecular structure of **1**. Selected bond lengths [Å] and angles [°]: C(12)–Br(2) 1.892(2), C(12)–Br(1) 1.873(3), C(12)–C(11) 1.318(4), C(11)–C(1) 1.445(4); Br(1)–C(12)–Br(2) 113.56(15), Br(2)–C(12)–C(11) 120.7(2), Br(1)–C(12)–C(11) 125.7(2), C(12)–C(11)–C(1) 130.8(2).

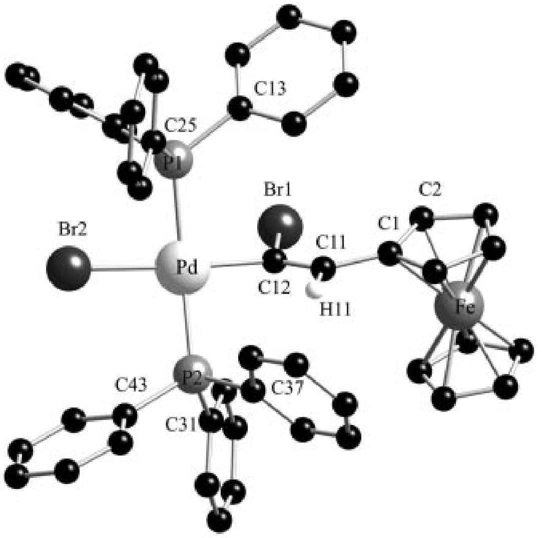


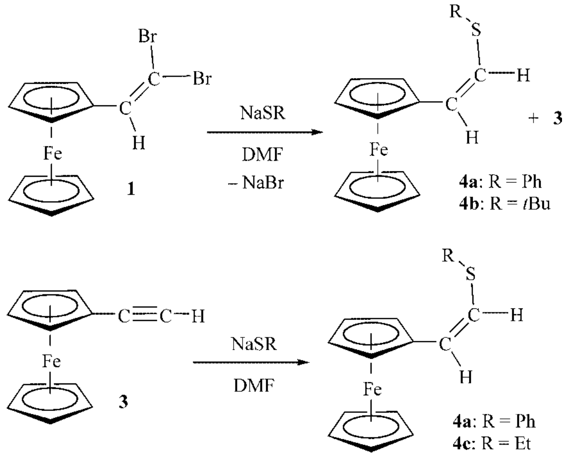
Figure 2. Ball-and-stick view of the molecular structure of **2**. For clarity, only the vinylic hydrogen atom is shown. Selected bond lengths [Å] and angles [°]: Pd–P(1) 2.3375(17), Pd–P(2) 2.3185(18), Pd–Br(2) 2.4479(8), Pd–C(12) 2.037(6), C(12)–Br(1) 1.952(6), C(12)–C(11) 1.272(9), C(11)–C(1) 1.481(8); P(1)–Pd–P(2) 166.74(5), Br(2)–Pd–C(12) 173.86(16), P(1)–Pd–C(12) 92.66(17), P(2)–Pd–C(12) 90.21(17), P(1)–Pd–Br(2) 84.76(4), P(2)–Pd–Br(2) 93.61(4), Br(1)–C(12)–Pd 108.8(3), Pd–C(12)–C(11) 120.4(5), C(12)–C(11)–C(1) 135.2(6).

Several experimental and theoretical studies have shown that the oxidative addition of vinyl halides to low-valent Pd^0 centres leads to Pd^{II} complexes bearing a σ-alkenyl ligand.[14–18] For example, treatment of $[Pd(PPh_3)_4]$ with β-bromostyrene results in the formation of *trans*-$[PdBr(CH{=}CHPh)(PPh_3)_2]$.[18] The vinyl bromide **1** adds oxidatively to $[Pd(PPh_3)_4]$ at 60 °C in toluene solution in a similar manner to produce the heterodinuclear σ-alkenyl complex *trans*-$[PdBr\{C(Br){=}C(H){-}Fc\}(PPh_3)_2]$ (**2**) in 76% yield (Scheme 1). The *trans* geometry of the PPh_3 ligands is evidenced by the presence of a single resonance at δ = 22.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Unfortunately, the reaction with $[Pt(PPh_3)_4]$ under identical conditions led mainly to the formation of *cis*-$[PtBr_2(PPh_3)_2]$.

The X-ray structure of **2**, which is shown in Figure 2, reveals a slightly deformed square-planar coordination around Pd consisting of two *trans* PPh_3 residues, a terminal bromo ligand and a vinylferrocene moiety. The C(11)–C(12) double bond in **2** is shorter than in **1** [1.318(4) vs. 1.272(9) Å]. The latter ligands are placed almost linearly, with a Br(2)–Pd–C(12) angle of 173.86(16)°. Due to a stereoselective activation of the Br(2)–C(12) bond during the oxidative addition process, the stereochemistry about the vinylic C(11)=C(12) double bond is *anti* (*E*) with respect to the ferrocene unit and the Pd centre, with a C(1)–C(11)–C(12)–Pd dihedral angle of 164.7°.

Reactivity of 1 Towards Various Thiolates

In the context of our work on the development of new dithioether ligands and their coordination chemistry,[19–21] we recently demonstrated that the nucleophilic attack of various thiolates on the π-conjugated 2-azabutadiene $[Cl_2C{=}C(H)N{=}CPh_2]$ in dmf affords the functionalised derivatives $[(RS)_2C{=}C(H){-}N{=}CPh_2]$ (R = Ph, *i*Pr) by replacement of the two vinylic chloro substituents by SR^-.[22] If the reaction with sodium thiophenolate is carried out in a 1:1 ratio, the monosubstituted product $[(PhS)(Cl)C{=}C(H){-}N{=}CPh_2]$ can be isolated. Unexpectedly, treatment of **1** with thiolates was less straightforward. Thus, when **1** is treated with just 1 equiv. of thiophenolate the reaction is incomplete and leads to the formation of a mixture of **1**, the substitution product **4a** and some ethynylferrocene (**3**). Treatment of **1** with a slight excess of NaSPh in dmf allowed us to isolate the vinylic thioether **4a** as an orange-red solid. However, the elemental analysis and NMR spectroscopic data of **4a** did not match the expected values for [(PhS)(Br)-C=C(H)–Fc] but instead suggested the formulation (*Z*)-[(PhS)(H)C=C(H)–Fc] (**4a**; Scheme 2). Treatment of **1** with an excess of NaS*t*Bu in dmf also did not lead to the anticipated dithioether compound [(tBuS)$_2$C=C(H)–Fc]. Instead, analysis of the crude product by TLC indicated the presence of (*Z*)-[(*t*BuS)(H)C=C(H)–Fc] (**4b**) together with a large amount of ethynylferrocene (**3**). The formation of ethynylferrocene, which was isolated by column chromatography, was unambiguously confirmed by an X-ray diffraction analysis.



Scheme 2.

The (*Z*) stereochemistry about the vinylic double bond of **4b** and the unexpected replacement of the Br substituent by an H atom were also confirmed by X-ray diffractometry. As illustrated in Figure 3, the crystallographic data unambiguously confirm the replacement of one bromine atom in the (*Z*) position relative to the ferrocene unit by an S*t*Bu group and replacement of the second bromine atom by a hydrogen atom. The Cp ring bearing the vinyl group and the thioether function are almost coplanar, with a C(10)–C(11)–C(12)–S torsion angle of 2.8°. We were unable to synthesise the corresponding SEt derivative (*Z*)-[(EtS)(H)-C=C(H)–Fc] (**4c**) by this method as, except for some minor amounts of the dithioether compound (*Z*)-[(EtS)(H)-C=C(SEt)–Fc] (**5c**; see below), only ethynylferrocene (**3**) could be isolated from this reaction. X-ray checks carried out on several differently shaped crystals and full analysis of one sample always showed the presence of ethynylferrocene.[23,24]

A related structural motif was recently crystallographically established for the vinylferrocene derivatives **A** and **B**, which were obtained after hydrolysis or alcoholysis of 2,3-diferrocenyl-1-(methylthio)cyclopropenylium iodide (Scheme 3).[25]

The formation of large amounts of ethynylferrocene can be rationalised by a dehydrobromination reaction induced by the basic thiolate reagent. It is well established that addition of thiolates (or thiols under basic conditions) across the C≡C bond of alkynes leads to vinyl thioethers.[26–30] For example, treatment of phenylacetylene with sodium *p*-toluenethiolate in dmf produces (*Z*)-1-phenyl-2-(*p*-tolylmercapto)ethene in a stereospecific manner. According to the kinetics of the reaction, a stepwise mechanism has been suggested for this addition which is initiated by nucleophilic attack of SR$^-$ at the β-carbon atom of Ph–C≡C–H, followed by protonation of the resulting carbanionic intermediate.[27] We therefore attempted an alternative synthesis of **4c** along this route by treating Fc–C≡C–H (**3**) with NaSEt in dmf at room temperature. Indeed, **4c** was now accessible in 78% isolated yield as a red crystalline solid after workup in aqueous solution. An X-ray diffraction study confirmed the (*Z*) disposition of the Fc moiety and the SEt substituent about the C=C bond (see Figure 4). As in **4b**, the Cp ring bearing the vinyl group and the thioether function are almost coplanar, with a C(10)–C(11)–C(12)–S torsion angle of 2.7°. The Cp rings of **4c** are again placed in an eclipsed conformation.

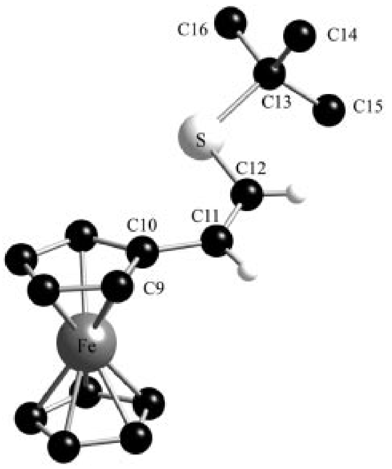
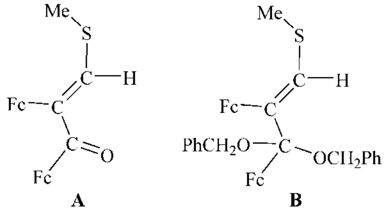


Figure 3. Ball-and-stick view of the molecular structure of **4b** showing the (*Z*) configuration around the C=C bond. For clarity, only the vinylic hydrogen atoms are shown. Selected bond lengths [Å] and angles [°]: C(10)–C(11) 1.458(7), C(11)–C(12) 1.351(8), C(12)–S 1.749(5), C(13)–S 1.845(5), C(13)–C(14) 1.545(7); C(9)–C(10)–C(11) 123.1(5), C(10)–C(11)–C(12) 128.8(5), C(11)–C(12)–S 125.0(4), C(12)–S–C(13) 103.0(3), C(14)–C(13)–S 110.1(3), C(15)–C(13)–S 110.8(4), C(16)–C(13)–S 103.5(4).



Scheme 3.

The complex (*Z*)-[(PhS)(H)C=C(H)–Fc] (**4a**) is also accessible by this route. The (*Z*) arrangement of the two vinylic hydrogen atoms of **4a** is corroborated by the ^{1}H NMR spectrum, which exhibits an AB pattern centred at δ = 6.31 ppm with a typical vicinal (*Z*) coupling constant of 10.1 Hz. Similar values (δ = 6.45 ppm, $^3J_{A,B}$ = 10.8 Hz) were recently reported for (*Z*)-[(PhS)(H)C=C(H)–C_6H_4O-Me].[31a] In contrast, a $^3J_{H,H}$ coupling constant of 15.3 Hz

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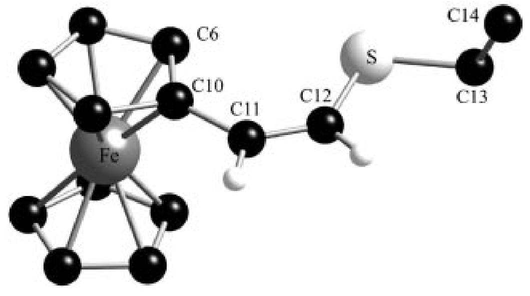
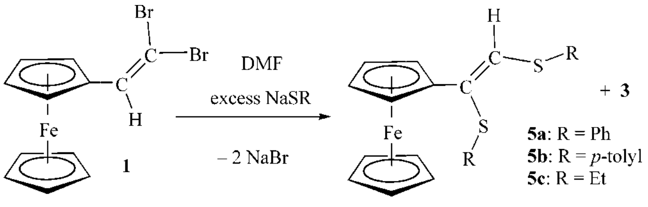


Figure 4. Ball-and-stick view of the molecular structure of **4c**. Selected bond lengths [Å] and angles [°]: C(10)–C(11) 1.463(7), C(11)–C(12) 1.314(7), C(12)–S 1.750(4), C(13)–S 1.789(6), C(13)–C(14) 1.522(5); C(10)–C(11)–C(12) 129.6(4), C(11)–C(12)–S 126.8(4), C(12)–S–C(13) 101.6(2), C(14)–C(13)–S 114.3(3).

has been reported for (*E*)-[(PhS)(H)C=C(H)–Ph], which was obtained by Rh-catalysed hydrothiolation of phenylacetylene.[31b] The NOESY spectrum (see Supporting Information) reveals a weak correlation between the unresolved Cp signal at δ = 4.62 ppm and the vinylic resonance at δ = 6.35 ppm, thereby proving the existence of a weak $^4J_{\mathrm{H,H}}$ "W-coupling".

With the aim of synthesising ferrocene-based dithioether ligands, complex **1** was treated with an excess of aromatic thiolate (10 equiv.) at room temperature. Although the vinylic dithioether complexes (*Z*)-[(ArS)(H)C=C(SAr)–Fc] (**5a**,**b**) were formed as orange-red solids, albeit in moderate yields (46–51%) due to a competing elimination reaction that produces ethynylferrocene (**3**; Scheme 4), a closer look at the NMR spectra of **5a**,**b** and the X-ray data for the heterodinuclear compound **6** (see Figure 5 for the rhenium dithioether complex) revealed that a rearrangement reaction again occurred.[32] The overall yield of **5c** was lower still (22%) with the more basic ethyl thiolate as nucleophile, giving **3** in more than 50% yield as the main product.



Scheme 4.

A literature survey indicates that this rearrangement has a precedent in organic chemistry. Thus, the mechanistic investigations of Truce and Boudakian on the reactivity of 1,1-dichloroethylene towards an excess of sodium *p*-toluenethiolate in EtOH demonstrate that this reaction affords exclusively (*Z*)-1,2-bis(*p*-tolylmercapto)ethene. The intermediacy of an alkyne species ArS–C≡CH was suggested to rationalize this interesting addition/elimination sequence.[33] Another research group later independently confirmed these findings with NaSPh as nucleophile and dmf as solvent.[34]

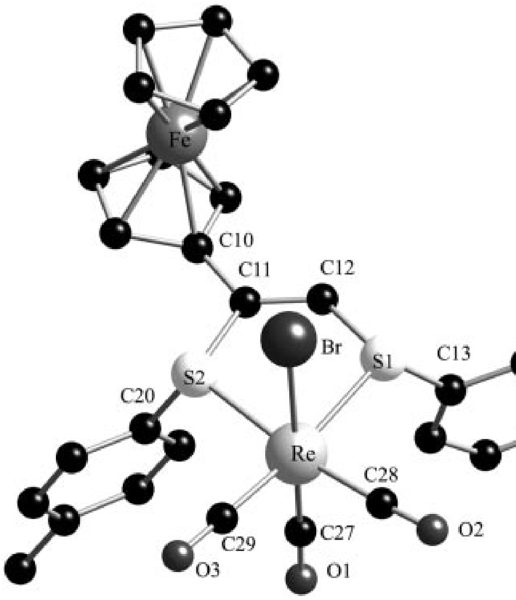
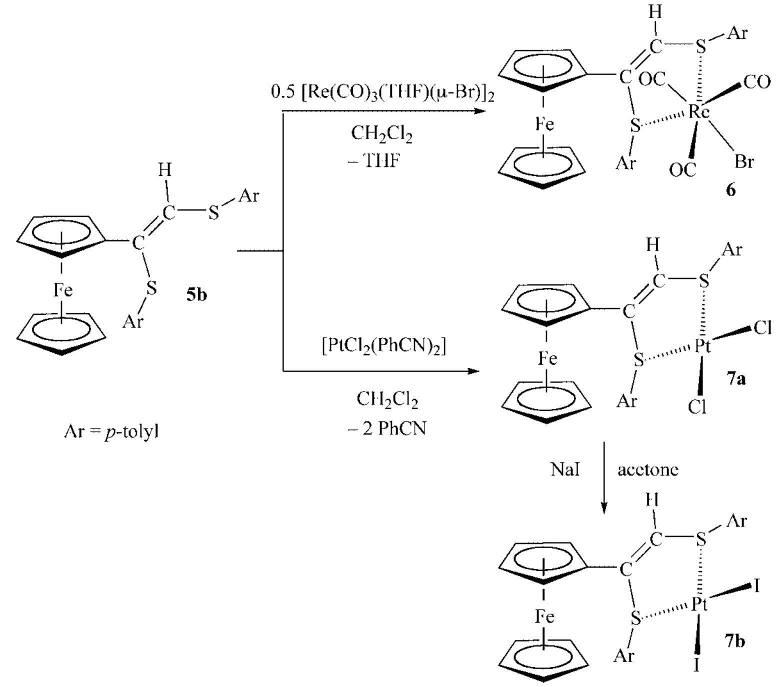


Figure 5. Ball-and-stick view of the molecular structure of **6**. Selected bond lengths [Å] and angles [°]: Re–S(1) 2.4705(18), Re–S(2) 2.4807(16), Re–Br 2.6304(8), Re–C(27) 1.908(8), Re–C(28) 1.944(9), Re–C(29) 1.947(9), C(12)–S(1) 1.755(7), C(11)–S(2) 1.807(7), C(12)–C(11) 1.331(9), C(11)–C(10) 1.466(9); Br–Re–C(27) 176.2(2), Br–Re–S(1) 79.42(5), Br–Re–S(2) 81.00(5), C(28)–Re–C(29) 90.2(3), C(28)–Re–S(1) 92.5(3), C(28)–Re–S(2) 172.5(2), C(29)–Re–S(2) 94.0(2), C(29)–Re–S(1) 172.7(2), C(10)–C(11)–C(12) 124.0(6), C(11)–C(12)–S(1) 126.9(6), C(12)–C(11)–S(2) 119.1(5), C(10)–C(11)–S(2) 116.8(5), C(12)–S(1)–C(13) 100.3(3), C(11)–S(2)–C(20) 101.3(3).

Coordination Chemistry of the Dithioether Ligand 5b

Preliminary studies demonstrated that dithioether compounds **5** can be used as chelating ligands to assemble heterodinuclear compounds.[35] Thus, reaction monitoring by IR spectroscopy revealed that treatment of dimeric $[\mathrm{Re(thf)(CO)_3(\mu\text{-}Br)}]_2$ with 2 equiv. of **5b** in CH_2Cl_2 solution led to formation of the brick-red complex [Fc{C(S–*p*-tolyl)=C(S–*p*-tolyl)(H)}–Re(Br)(CO)$_3$] (**6**; Scheme 5) almost quantitatively, within 15 min. The facial arrangement of the carbonyl groups of air-stable **6** can be deduced from the observation of three ν(CO) vibrations in KBr at 2031, 1958 and 1930 cm^{-1}.

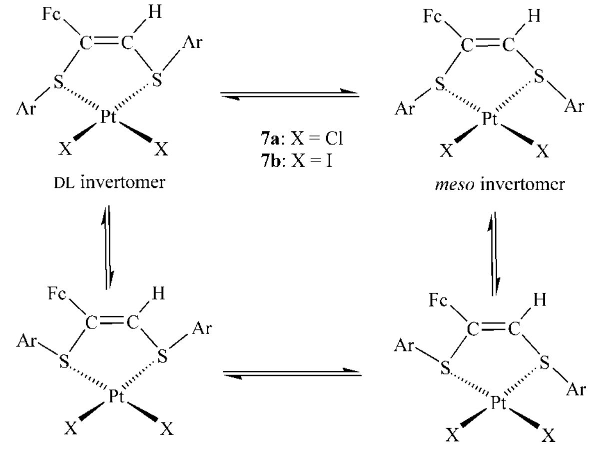
The rearrangement discussed above, which results in a (*Z*) substitution of C(11) and C(12) by S–*p*-tolyl groups, was corroborated by an X-ray diffraction study. Figure 5 reveals that the octahedral coordination around the Re centre is achieved by three carbonyl groups, a chelating dithioether ligand and a bromo ligand, thus conferring an 18-electron count at the Re$^{\mathrm{I}}$ centre. The bromo substituent and the ferrocenyl moiety of the dithioether ligand are directed in the same sense. The dithioether ligand forms a five-membered ring with mean Re–S bond lengths of 2.4807 Å, which are somewhat shorter than those found for *fac*-[{(PhSCH$_2$)$_2$SiPh$_2$}Re(Br)(CO)$_3$] (2.515 Å).[36] Like in the latter compound, the aryl rings of the thioether groups are



Scheme 5.

both *syn*-orientated and form a *meso* invertomer, although they point in the opposite direction to the bromo ligand.[36,37]

Similarly, treatment of $[PtCl_2(PhCN)_2]$ with a slight excess of **5b** yielded the brownish air-stable square-planar dithioether complex [Fc–{C(S–*p*-tolyl)=C(S–*p*-tolyl)-(H)}$PtCl_2$] (**7a**). The spectroscopic and elemental analysis data are in agreement with a bidentate chelating coordination mode of **5b** at the platinum atom, similar to that encountered in *cis*-[MCl_2(MeSCH=CHSMe)] (M = Pd, Pt) and other related Pd^{II} and Pt^{II} compounds.[38] Metathesis with NaI in acetone solution converted **7a** into red-brown [Fc–{C(S–*p*-tolyl)=C(S–*p*-tolyl)(H)}PtI_2] (**7b**), whose FAB^+ mass spectrum displays the peak for the molecular ion. The ^1H NMR spectrum of **7a** recorded at 293 K displays a rather broad unresolved signal between δ = 4.80 and 4.10 ppm for the Cp resonances; the vinylic proton gives rise to a very broad hump centred at δ = 6.41 ppm. At 213 K, the vinylic proton appears sharper at δ = 6.54 ppm and the Cp protons give rise to several signals in the range δ = 4.58–3.92 ppm. This temperature-dependent behaviour is most probably due to a pyramidal inversion process operating for the two sulfur atoms that gives rise to *meso* and DL invertomers, as outlined in Scheme 6. Since this phenomenon has been studied by us and several other groups in the past,[20a,21a,36a,39] we did not undertake a detailed kinetic variable-temperature study. In contrast, the diiodo analogue **7b** displays well-resolved signals at room temperature, which barely sharpen upon heating to 313 K. This indicates a fast exchange such that only one "averaged planar" conformation is observed on the NMR timescale.



Scheme 6.

The vinylic proton signal at δ = 6.32 ppm exhibits a $^3J_{Pt,H}$ coupling of 73 Hz, and two distinct singlets are observed at δ = 2.41 and 2.34 ppm in a 1:1 ratio for the methyl groups of the *p*-tolyl rings. We and others have previously noted this finding for various PtX_2 complexes ligated with chelating dithioethers. The enhanced thermodynamic *trans* influence of I over Cl elongates the Pt–S bonds (as corroborated by several X-ray structures), and the concomitant weakening of the metal–sulfur bonds accounts for the lower activation barrier of the inversion process.[20a,20b,21,39]

Electrochemistry

The anodic sweep of **1** in MeCN between –0.25 and +0.75 V vs. Ag/Ag^+ on a Pt electrode leads to a totally reversible peak in the cyclic voltammogram (CV), even for low scan rates (i.e. 100 mV s^{-1}). The separation between the anodic and cathodic peaks is about 60 mV, which indicates a fast electron transfer. The peak potential for **1** is about +0.25 V vs. Ag/Ag$^+$. In comparison with the corresponding peak values measured for the non-substituted ferrocene/ferrocenium couple (E_p = 0.21 V vs. Ag/Ag$^+$) or the vinylferrocene/ferrocenium couple (E_p = 0.24 V vs. Ag/Ag$^+$), the introduction of the CH=CBr$_2$ group does not significantly change the oxidation peak potential.[40a]

The CV of **2** in MeCN exhibits a reversible one-electron oxidation peak at +0.08 V vs. Ag/Ag$^+$ (i_{pc}/i_{pa} = 1, ΔE = 60 mV; see Supporting Information). This oxidation is "easier" (i.e. occurs at lower positive potential) than that for precursor **1** due to the electronic communication with the electron-rich Pd(PPh$_3$)$_2$Br moiety. A contribution from a Pd(PPh$_3$)$_2$Br motif was recently observed in (vinylferrocene)Pd^{II} complexes containing thiophene spacers of the type [(C$_5$H$_5$)Fe(C$_5$H$_4$CH=CH–th–Pd(PPh$_3$)$_2$(Br)] (th = 2,5-disubstituted thiophene).[41] The potentials of these complexes were reported to be lower than those without an end-capping Pd(PPh$_3$)$_2$Br unit, thereby implying the delocalisation of Pd electron density into the spacer chain through a dπ→pπ interaction. This behaviour is also observed for dithioether **5b**. The CV of **5b** between –0.25 and +0.50 V vs. Ag/Ag$^+$ on a Pt electrode at 100 mV s^{-1} reveals the presence of a reversible peak also involving a fast electron transfer (see Supporting Information). Since this ferrocene derivative bears two electron-donating substituents, the oxidation is "easier" than that for **1**. The potential of the reversible peak for **5b** (E_p = 0.19 V vs. Ag/Ag$^+$) is lower than that for **1**. Oxidation of **7a** between 0.00 and +0.60 V vs. Ag/Ag$^+$ on a platinum electrode at 100 mV s^{-1} again leads to a reversible signal (see Supporting Information). Actually, the complexation of **5b** with a PtCl$_2$ fragment decreases the electronic density on the ferrocene moiety and the oxidation peak is therefore shifted towards higher oxidation potentials with respect to that for **1** and **5b**. The E^0 value (E_p = 0.39 V vs. Ag/Ag$^+$) is larger than that for compound **1**. This behaviour is also observed for compound **6**. The E^0 value for the couple **6/6$^{\cdot+}$** (E_p = 0.33 V vs. Ag/Ag$^+$) is in the same range as that for the couple **7a/7a$^{\cdot+}$** (E_p = 0.39 V vs. Ag/Ag$^+$). A shift after complexation with metal centres has also been noted previously for other ferrocene-based thioether ligands.[35e]

The CV of **5b** between –0.40 and +2.00 V vs. Ag/Ag$^+$ on a Pt electrode at 100 mV s^{-1} reveals a different shape of the voltammogram curve (Figure 6). Thus, we now observe three irreversible waves at 0.19, 1.16 and 1.29 V vs. Ag/Ag$^+$. The first irreversible wave corresponds to the oxidation of the ferrocene moiety. Surprisingly, the lifetime of the ferrocenium radical cation formed during the oxidation in this experiment is not long enough to be observed during the reversible scan. This behaviour is usually not observed for ferrocenium radical cations. This phenomenon is probably due to the low scan rate and the high value of the final potential. Partial peak reversibility is again observed when we increase the scan rate to 200 mV s^{-1}. The CV of **7a** between –0.40 and +2.00 V vs. Ag/Ag$^+$ at a Pt electrode at 100 mV s^{-1} leads to a voltammogram similar to that of **5b** (see Supporting Information). However, the two irreversible peaks in this voltammogram obtained after oxidation of the two S-*p*-tolyl substituents are less well-defined than that for **5b**. Moreover, the ferrocenium radical cation of **7a** is more stable than the corresponding radical cation of **5b**. In fact, we observe a partial reversibility of the first oxidation peak, even at low scan rate (100 mV s^{-1}).

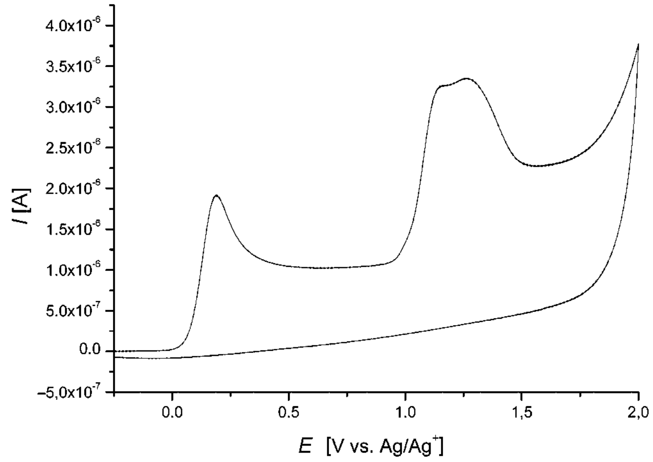


Figure 6. CV of **5b** (1 mM) in CH$_2$Cl$_2$ + Bu$_4$NPF$_6$ (0.1 M) at 100 mV s^{-1} at a platinum electrode.

The same electrochemical measurements were also performed using glassy carbon electrodes. All voltammograms are very similar. The only difference observed between platinum and carbon electrodes concerns the value of E_p (Table 1).

Table 1. Values of standard potentials or peak potentials for monomer/radical cation in dichloromethane (vs. Ag/Ag$^+$) deduced from CV measurements.

Compound	E_p [V] on Pt electrode	E_p [V] on C electrode
1	0.25	0.25
2		0.08
5b	0.19, 1.16, 1.19	0.13, 1.21
6	0.33, 1.61	0.32, 1.59
7	0.39, 1.72	0.36, 1.59

Solid-State Luminescence of 5b and 6

When excited at 270 nm, the solid-state emission spectra of **5b** and the heterometallic system **6** (Figure 7) at room temperature are quite similar, with a broad band at 668 and 670 nm, respectively. This band is tentatively assigned to an intraligand transition. More importantly, the incorporation of ferrocene and its derivatives in a luminescent system produced effective quenchers of excited states by energy-transfer processes.[42a] These compounds are known for their capacity to inhibit the lowest energy states of a number of molecules frequently used as photosensitizers.[42b,42c] This finding may also explain the luminescence quenching of the rhenium fragment in compound **6**.

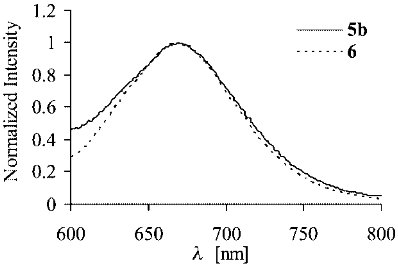


Figure 7. Corrected and normalised solid-state luminescence spectra recorded at room temperature for compounds **5b** (solid) and **6** (dotted).

Conclusion and Perspectives

This study has demonstrated that the reactivity of **1** towards thiolates is not trivial. We are currently investigating these rearrangement reactions in more detail {isolation of intermediates, influence of temperature and solvent, utilisation of [Cl_2C=C(H)–Fc] instead of [Br_2C=C(H)–Fc] as starting material, use of other aromatic substrates such as (dibromovinyl)[2.2]paracyclophane, …} to develop a clear mechanistic understanding of these interesting transformations. Moreover, the preparation of π-conjugated thioether ligands **4** and **5** allows a promising development in organometallic coordination chemistry. We are currently working on the synthesis, reactivity and electrochemical investigation of other neutral and ionic complexes ligated by **4** and **5**. Furthermore, the substitution of the bromo substituents of **1** by $^{-}$OR, $^{-}NR_2$ or $^{-}PR_2$ may also lead to promising new ligand systems.

Experimental Section

General: All reactions were performed using a conventional vacuum/argon line with standard Schlenk techniques. (2,2-Dibromovinyl)ferrocene (**1**), [$Pd(PPh_3)_4$], [Re(μ-Br)$(CO)_3$(thf)$]_2$ and [$PtCl_2(PhCN)_2$] were prepared according to literature methods.[13,43] Thiophenol, *p*-thiocresol, 2-methyl-2-propanethiol and ethanethiol were purchased from commercial sources and used without further purification. All solvents were distilled from appropriate drying agents. IR spectra were recorded with a Nicolet Nexus 470 spectrometer. All NMR spectra were recorded in $CDCl_3$ with a Bruker AC 300 (^{1}H: 300.13 MHz; ^{13}C: 75.48 MHz; ^{31}P: 121.49 MHz) using the solvent as reference, except for ^{31}P, where the chemical shifts are quoted relative to 85% H_3PO_4 in D_2O. UV/Vis spectra were recorded with a Varian Cary 50 spectrophotometer. The solid-state emission spectra were recorded at room temperature with a Jobin–Yvon Fluorolog-3 spectrometer using a cylindrical quartz capillary (diameter: 0.5 cm) with a scan speed of 1 nm s^{-1}. Intensity scales are presented in arbitrary units. The FAB$^+$ mass spectrum of **7b** was obtained with a VG Autospec spectrometer using NBA as matrix.

Electrochemical Setup: Analytical experiments were performed in a three-compartment cell fitted with an $AgClO_4$ (0.1 M in CH_3CN)| Ag reference electrode, a glassy carbon electrode (diameter: 3 mm) or a Pt electrode (diameter: 1 mm) and a platinum counter electrode. The electrochemical apparatus was an Autolab PGSTAT 20 Potentiostat Galvanostat (Ecochemie). The solvent was spectroscopic grade CH_2Cl_2 or acetonitrile with [Bu_4N][PF_6] (TBAF) as supporting electrolyte. The concentration of the monomeric substrate was 10^{-3} M. Under these conditions, the $E_{1/2}$ of $Cp_2Fe^{+/0}$ was found to be 0.21 V ± 0.01 V (CH_2Cl_2) vs. an Ag reference.

Preparation of *trans*-[$(PPh_3)_2$PdBr{C(Br)=C(H)–Fc}] (2): Compound **1** (185 mg, 0.5 mmol) was added to a suspension of [$Pd(PPh_3)_4$] (520 mg, 0.45 mmol) in toluene (15 mL) and the mixture was warmed to 60 °C for 1 d. The resulting clear, red solution was then concentrated to 8 mL and layered with heptane. Complex **2** crystallised as red needles after storing this solution in a refrigerator overnight. Yield: 76% (380 mg). ^{1}H NMR: δ = 7.77 (m, 10 H, Ph), 7.17–7.41 (m, 20 H, Ph), 6.09 (s, 1 H, H_{vinyl}), 3.93 (m, 2 H, Cp), 3.81 (m, 2 H, Cp), 3.72 (s, 5 H, Cp) ppm. ^{31}P{^{1}H} NMR: δ = 22.7 (s) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 229 nm (62800 M^{-1}cm^{-1}), 310 (13100), 365 (13600). $C_{48}H_{40}Br_2FeP_2Pd$ (1000.9): calcd. C 57.60, H 4.03; found C 57.48, H 4.09.

Typical Procedure for the Conversion of the Dibromo Olefin 1 into 4a–c and 5a–c: Compound **1** (1 mmol) was stirred with an excess of thiolate (10 mmol) in dry dmf (10 mL) at room temperature for 1 d. The reaction mixture was then poured into water (10 mL). The organic layer was extracted with Et_2O (2 × 25 mL), washed with brine (20 mL) and water (2 × 25 mL) and dried with Na_2SO_4. Evaporation of the solvents gave the crude products. Purification was carried out by chromatography on silica gel. In the case of treatment of **1** with 4 equiv. of thiolates, the ratios of thioether compounds **4a/3** and **4b/3** were both 25%/75%.

FcCH=CH(SPh) (4a): Eluent: CH_2Cl_2/petroleum ether (1:9). M.p. 50 °C. ^{1}H NMR: δ = 7.25–7.52 (m, 5 H, Ph), 6.35 (d, $^3J_{H,H}$ = 10.1 Hz, 1 H, $H_{A,vinyl}$), 6.26 (d, $^3J_{H,H}$ = 10.1 Hz, 1 H, $H_{B,vinyl}$), 4.62 (br. s, 2 H), 4.27 (br. s, 2 H, Cp), 4.16 (s, 5 H, Cp) ppm. ^{13}C{^{1}H} NMR: δ = 68.9, 69.2, 69.3, 80.8 (*Cp*HC=), 121.0 (CpH*C*=), 126.5, 126.8, 129.0, 129.3 [C-14, C-15, C-16, C-17, C-18, =*C*H(SPh)], 136.6 (C-13) ppm. $C_{18}H_{16}FeS$ (320.23): calcd. C 67.51, H 5.04, S 10.01; found C 67.42, H 5.74, S 9.80.

FcCH=CH(S*t*Bu) (4b): Eluent: CH_2Cl_2/petroleum ether (1:9). Yield: 52% (156 mg). M.p. 50–52 °C. ^{1}H NMR: δ = 6.19 (d, $^3J_{H,H}$ = 10.0 Hz, 1 H, $H_{A,vinyl}$), 6.11 (d, $^3J_{H,H}$ = 10.0 Hz, 1 H, $H_{B,vinyl}$), 4.58 (br. s, 2 H, Cp), 4.23 (br. s, 2 H, Cp), 4.15 (s, 5 H, Cp), 1.43 (s, 9 H, CH_3) ppm. ^{13}C{^{1}H} NMR: δ = 30.9 (CH_3), 43.8 [*C*-$(CH_3)_3$], 68.5, 69.1, 69.2, 81.9 (*Cp*HC=), 119.5 (CpH*C*=), 124.1 [=*C*H(S*t*Bu)] ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 229 (16200), 251 (10500), 298 (9100), 351 (7100), 452 nm (3900 M^{-1}cm^{-1}). $C_{16}H_{20}FeS$ (300.23): calcd. C 64.00, H 6.67, S 10.67; found C 63.98, H 6.58, S 10.62.

FcCH=CH(SEt) (4c): Eluent: petroleum ether. M.p. 38–39 °C. ^{1}H NMR: δ = 6.14 (d, $^3J_{H,H}$ = 10.4 Hz, 1 H, $H_{A,vinyl}$), 5.95 (d, $^3J_{H,H}$ = 10.4 Hz, 1 H, $H_{B,vinyl}$), 4.32 (br. s, 2 H, Cp), 4.24 (br. s, 2 H, Cp), 4.12 (s, 5 H, Cp), 2.75 (q, $^3J_{H,H}$ = 7.4 Hz, 2 H, S$CH_2$$CH_3$), 1.22 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, S$CH_2$$CH_3$) ppm. UV/Vis ($CH_2Cl_2$): λ_{max} (ε) = 229 (11500), 250 (9200), 298 (10900), 351 (550), 452 nm (350 M^{-1}cm^{-1}). $C_{14}H_{16}FeS$ (272.18): calcd. C 61.76, H 5.88, S 11.76; found C 61.68, H 5.73, S 11.67.

Alternative Preparation of 4a and 4c: Ethynylferrocene (210 mg, 1 mmol) was added to a stirred solution of thiolate (10 mmol) in dmf (10 mL). The solution was stirred at room temperature for 1 d and then poured into water. The organic layer was extracted with diethyl ether, washed with water (5 mL) and brine (2 × 5 mL) and dried with Na_2SO_4. Solvent evaporation provided the crude products. Column chromatography with petroleum ether as eluent afforded 207 mg of **4a** (yield: 76%) and 249 mg of **4c** (yield: 78%).

FcC(SPh)=CH(SPh) (5a): Obtained by column chromatography on silica gel with petroleum ether as eluent (197 mg, 46%). ^{1}H NMR:

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δ = 4.17 (s, 5 H, Cp), 4.23 (s, 2 H, Cp), 4.48 (br. s, 2 H, Cp), 7.13 (s, 1 H, H_{vinyl}), 7.23–7.52 (m, 10 H, Ph) ppm. $^{13}C\{^{1}H\}$ NMR: δ = 69.3, 69.8, 70.1 (C-1–C-9), 79.7 (C-10), 123.5, 125.6, 127.1, 127.3, 127.4, 129.0, 129.2, 129.9, 130.1, 130.7, 132.2, 134.7, 135.0, 135.5, 135.9, 141.2 (C-11–C-24) ppm. $C_{24}H_{20}FeS_2$ (428.39): calcd. C 67.29, H 4.67, S 14.95; found C 67.18, H 4.59, S 14.83.

FcC(S–*p*-tolyl)=CH(S–*p*-tolyl) (5b): Eluent: petroleum ether/CH_2Cl_2 (9:1). Yield: 51% (230 mg). M.p. 135–136 °C. ^{1}H NMR: δ = 7.30–7.00 (m, 9 H, C_6H_4 + H_{vinyl}), 4.40 (br. s, 2 H, Cp), 4.15 (br. s, 2 H, Cp), 4.09 (s, 5 H, Cp), 2.31 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3) ppm. $^{13}C\{^{1}H\}$ NMR: δ = 21.3, 21.4 (CH_3), 67.2, 69.2, 69.9 (Cp), 87.5 (CpH*C*=), 128.0, 128.1, 128.9, 130.1, 130.3, 130.9, 132.4, 132.8, 133.2, 135.8 (C_6H_4), 137.7 [=*C*($SC_6H_4CH_3)_2$] ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 229 (64100), 257 (32200), 330 nm (9100 $M^{-1}cm^{-1}$). $C_{26}H_{24}FeS_2$ (456.44): calcd. C 68.42, H 5.30, S 14.05; found C 68.48, H 5.38, S 14.12.

FcC(SEt)=CH(SEt) (5c): Obtained by column chromatography on silica gel with petroleum ether as eluent (134 mg, 22%). ^{1}H NMR: δ = 6.26 (s, 1 H, H_{vinyl}), 4.53 (br., 2 H, Cp), 4.29 (s, 2 H, Cp), 4.11 (s, 5 H, Cp), 2.85 (m, 4 H, SCH_2CH_3), 2.77 (m, 4 H, SCH_2CH_3), 1.29 (m, 3 H, SCH_2CH_3), 1.27 (m, 3 H, SCH_2CH_3) ppm. $C_{16}H_{20}FeS_2$ (332.31): calcd. C 57.83, H 6.07, S 19.30; found C 57.78, H 5.93, S 19.18.

[FcC(S–*p*-tolyl)=C(H)(S–*p*-tolyl)$_2$Re(Br)(CO)$_3$] (6): [Re(μ-Br)(CO)$_3$(thf)]$_2$ (127 mg, 0.15 mmol) was added in several portions to a solution of **5b** (136 mg, 0.3 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature for 2 h and then concentrated to 3 mL under reduced pressure. Layering with heptane gave red needles after several days at 5 °C. Yield: 92% (119 mg). IR (KBr): ν(CO) = 2031 (vs), 1958 (s), 1931 (vs) cm^{-1}. ^{1}H NMR: δ = 7.37–7.27 (m, 8 H, C_6H_4), 7.07 (s, 1 H, H_{vinyl}), 4.83 s, (br., 2 H, Cp), 4.45 (br. s, 2 H, Cp), 4.55 (s, 5 H, Cp), 2.40 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 231 (47800), 300 (16100), 382 (2200), 482 nm (1700 $M^{-1}cm^{-1}$). $C_{29}H_{24}BrFeReO_3S_2{\cdot}0.5CH_2Cl_2$ (849.09): calcd. C 41.72, H 2.95; found C 41.85, H, 3.00.

[FcC(S–*p*-tolyl)=C(H)(S–*p*-tolyl)PtCl$_2$] (7a): [PtCl$_2$(PhCN)$_2$] (127 mg, 0.3 mmol) was added in several portions to a solution of **5b** (136 mg, 0.3 mmol) in CH_2Cl_2 (8 mL). The reaction mixture was stirred at room temperature for 4 h and then concentrated to 5 mL under reduced pressure. Addition of light petroleum gave an orange powder, which was filtered off and dried under vacuum. Yield: 91% (197 mg). ^{1}H NMR (213 K): δ = 7.79–7.30 (m, 8 H, C_6H_4), 6.54 (br. s, 1 H, H_{vinyl}), 4.58–3.92 (m, 9 H, Cp), 2.40 (br. s, 3 H, CH_3), 2.36 (br. s, 3 H, CH_3) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 228 (69500), 295 (20200), 382 (2400), 487 nm (1600 $M^{-1}cm^{-1}$). $C_{26}H_{24}Cl_2FePtS_2$ (722.43): calcd. C 43.23, H 3.35, S 8.88; found C 43.02, H 3.12, S 8.54.

[FcC(S–*p*-tolyl)=C(H)(S–*p*-tolyl)PtI$_2$] (7b): NaI (150 mg, 10 mmol) was added to a solution of **7a** (72 mg, 0.1 mmol) in acetone (5 mL). The reaction mixture was stirred at room temperature for 1 d and then the solvent was evaporated under reduced pressure. Extraction of the crude product with CH_2Cl_2 (4 mL) and addition of heptane gave an orange powder, which was filtered off and dried under vacuum. Yield: 90% (76 mg). ^{1}H NMR: δ = 7.68–7.19 (m, 8 H, C_6H_4), 6.32 (br. s, $^{3}J_{Pt,H}$ = 73 Hz, 1 H, H_{vinyl}), 4.53–4.09 (m, 9 H, Cp), 2.41 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3) ppm. FAB^{+} (NBA): *m*/*z* = 906.1 [M^{+}]. $C_{26}H_{24}FeI_2PtS_2$ (905.34): calcd. C 34.49, H 2.67; found C 34.12, H 2.76.

X-ray Crystallography: Crystal data and experimental details are given in Table 2. Data for **2** and **6** were collected with a Stoe IPDS diffractometer at 173(2) (**2**) and 193(2) K (**6**). The intensities were determined and corrected with the program INTEGRATE in IPDS (Stoe & Cie, 1999). An empirical absorption correction was employed using the FACEIT program in IPDS (Stoe & Cie, 1999). Data for **1** and **4b**,**c** were collected with a Bruker APEX-CCD (D8

Table 2. X-ray crystallographic and refinement data for **1**, **2**, **4b**, **4c** and **6**.

	1	**2**	**4b**	**4c**	**6**
Empirical formula	$C_{12}H_{10}Br_2Fe$	$C_{48}H_{40}Br_2FeP_2Pd$	$C_{16}H_{20}FeS$	$C_{14}H_{16}FeS$	$C_{29}H_{24}BrFeO_3ReS_2$
Formula mass [g mol^{-1}]	369.87	1000.81	300.23	272.18	806.56
T [K]	173(2)	173(2)	193(2)	173(2)	193(2)
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*Pbca*	$P2_1/n$	$P2_1/n$	*C*2/*c*	$P2_1/c$
a [Å]	7.5029(5)	20.385(5)	5.9214(12)	31.07(3)	10.169(2)
b [Å]	17.1025(11)	7.6128(12)	10.199(2)°	10.509(6)	25.404(5)
c [Å]	18.1892(12)	29.280(5)	12.232(2)°	7.457(9)	11.609(2)
β [°]	90	109.21(3)	96.88	91.42(3)	107.25(3)
V [Å^3]	2334.0(3)	4035.4(14)	733.4(3)	2463(4)	2864.2(10)
Z	8	4	2	8	4
$\rho_{calcd.}$ [Mg m^{-3}]	2.105	1.647	1.359	1.468	1.870
μ [mm^{-1}]	8.101	2.899	1.150	1.362	6.298
F(000)	1424	2000	316	1136	1560
Θ range [°]	2.24–26.43	2.39 –25.00	2.61–25.00	1.31–26.99	2.10–26.99
Index ranges	$-9 \le h \le 9$ $-21 \le k \le 21$ $-22 \le l \le 22$	$-10 \le h \le 10$ $-45 \le k \le 45$ $-14 \le l \le 14$	$-7 \le h \le 7$ $-12 \le k \le 12$ $-14 \le l \le 14$	$-39 \le h \le 39$ $-13 \le k \le 13$ $-9 \le l \le 9$	$-12 \le h \le 12$ $-29 \le k \le 32$ $-14 \le l \le 8$
Collected reflections	46927	24804	6312	16681	12577
Independent reflections	2409 [*R*(int) = 0.0430]	7081 [*R*(int) = 0.0654]	2559 [*R*(int) = 0.0515]	2693 [*R*(int) = 0.0287]	6127 [*R*(int) = 0.0529]
Data/restraints/parameters	2409/0/136	7081/0/487	2559/1/166	2693/0/146	6127/0/336
Largest difference peak/hole [e Å^{-3}]	0.663 and –0.377	1.027 and –1.036	0.8026 and 0.6562	0.7724 and 0.6119	1.704 and –1.816
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0260 wR_2 = 0.0622	R_1 = 0.0517 wR_2 = 0.1296	R_1 = 0.0551 wR_2 = 0.1410	R_1 = 0.0335 wR_2 = 0.0952	R_1 = 0.0474 wR_2 = 0.1140
R indices (all data)	R_1 = 0.0327 wR_2 = 0.0652	R_1 = 0.0726 wR_2 = 0.1412	R_1 = 0.0586 wR_2 = 0.1445	R_1 = 0.0370 wR_2 = 0.1058	R_1 = 0.0646 wR_2 = 0.1212
GOF on F^2	1.067	1.045	1.023	1.027	1.036

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three-circle goniometer, Bruker AXS) at 173(2) K; data collection, cell determination and refinement: Smart version 5.622 (Bruker AXS, 2001); integration: SaintPlus version 6.02 (Bruker AXS, 1999); empirical absorption correction: Sadabs version 2.01 (Bruker AXS, 1999). All structures were solved applying direct and Fourier methods, using SHELXS-90 and SHELXL-97.[44] For each structure, the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were placed in geometrically calculated positions and each was assigned a fixed isotropic displacement parameter based on a riding model. Refinement of the structures was carried out by full-matrix least-squares methods based on F_o^2 using SHELXL-97. CCDC-644866 to -644869 (for **1**, **2**, **4c**, **6**), -646158 (for **3**), and -650184 (for **4b**) 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.

Supporting Information (see footnote on the first page of this article): Crystallographic data and view of the structure and packing of **3** (Figure S1). Cyclic voltammograms of **2**, **5b** and **7a** are depicted in Figures S2–S5. Figures S6–S10 show the thermal ellipsoid plots of **1**, **2**, **4b**, **4c** and **6**. The NOESY ^{1}H NMR spectrum of **4a** is shown in Figure S11.

Acknowledgments

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