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Palladium and Platinum Complexes with Planar Chiral 1,2-disubstituted ferrocenes containing phosphine and thioether donor groups[†]

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[†] Dedicated to the memory of F. Albert Cotton, a caring mentor and a good friend

Summary

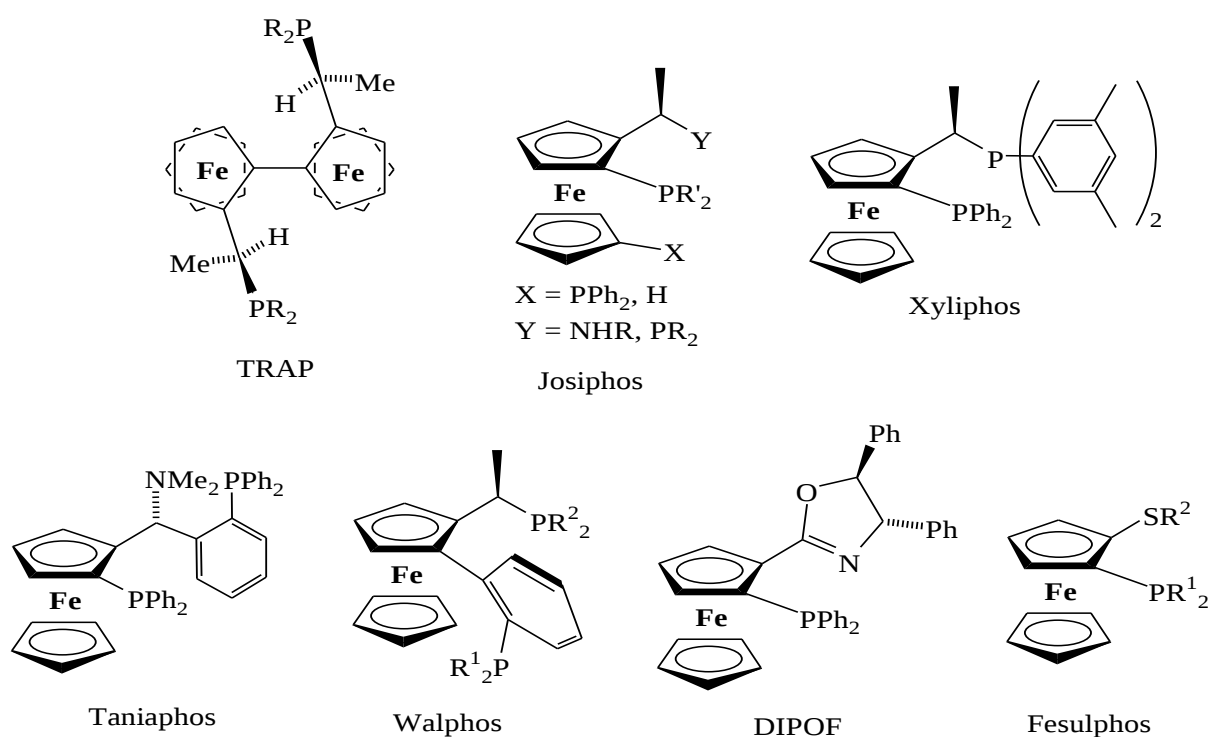
Three palladium(II) complexes and four platinum(II) complexes having general formula $\text{CpFe}\{1,2\text{-C}_5\text{H}_3(\text{PPh}_2)(\text{CH}_2\text{SR})\}\text{MCl}_2$ ($\text{M} = \text{Pd}$, $\text{R} = \text{Ph}$, Et and $t\text{Bu}$; $\text{M} = \text{Pt}$, $\text{R} = \text{Ph}$, Et , $t\text{Bu}$ and Cy) have been synthesized by reaction of the corresponding $\text{CpFe}\{1,2\text{-C}_5\text{H}_3(\text{PPh}_2)(\text{CH}_2\text{SR})\}$ ligands with $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ or $\text{PtCl}_2(\text{CH}_3\text{CN})_2$. These complexes have been fully characterized in solution and in solid state. In all cases, monomeric square planar complexes were obtained as pure diastereoisomers.

Keywords

Palladium, Platinum, ferrocene chemistry, planar chirality, phosphine ligands, thioether ligands.

Introduction

Since its discovery and early studies, which actively involved F. A. Cotton [1, 2], ferrocene has come a long way as a tool in chemistry, comprising applications in electrochemistry [3], material science [4-6], synthesis, and catalysis, particularly enantioselective catalysis by way of the planar chirality [7] associated to an asymmetric 1,2-disubstitution [8]. Important examples (see Scheme 1) are P,P ligands like TRAP [9-13], Josiphos [14], and particularly the industrially important Xyliphos [15], Taniaphos [16-18] and Walphos-type [19] ligands, (P,N) ligands, especially phosphine-oxazolines like, for instance DIPOF [20], and more recently (P,S) ligands like Fesulphos [21].



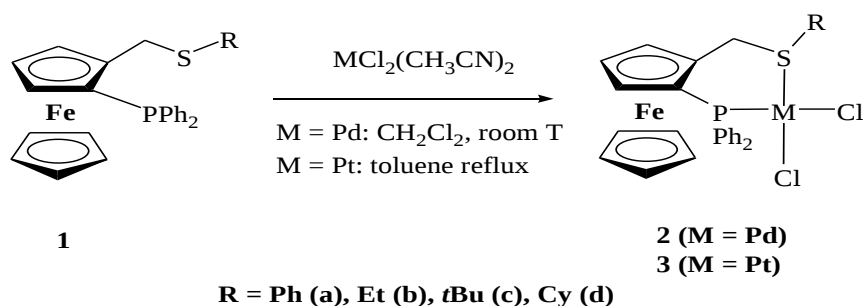
Scheme 1

We have recently developed new chiral ferrocenyl (P,S) ligands with general formula $\text{CpFe}\{1,2\text{-C}_5\text{H}_3(\text{PPh}_2)(\text{CH}_2\text{SR})\}$ [22], characterized by having only planar chirality, in both

racemic and enantiomerically pure forms (R or S configuration) [23] and briefly reported on their coordination chemistry [24, 25]. These ligands could be successfully applied to a few asymmetric catalytic reactions, namely palladium-catalyzed allylic substitution [22, 26] and iridium-catalyzed ketone hydrogenation [27]. In this paper we report on the synthesis and characterization of Pd^{II} and Pt^{II} complexes containing a variety of these (P,S) ligands. A useful aspect of this work is the structural verification of a systematic control of the coordinated sulphur atom chirality by the ferrocene absolute configuration, which is expected to be key in the transmission of the chiral information to the catalytic metal.

Results and Discussion

The synthetic procedures involved a ligand exchange process on the appropriate MCl₂(MeCN)₂ precursor (M = Pd, Pt), replacing the two MeCN ligands with the desired racemic (P,S) ligand, see Scheme 2. Four thioether ligands were used for this study, having phenyl, ethyl, *tert*-butyl and cyclohexyl as substituents on the sulphur atom. The reaction takes place in dichloromethane at room temperature for the palladium systems, whereas it requires much harsher conditions (toluene reflux) for platinum, in agreement with the greater lability of Pd^{II} for ligand exchange processes. Dark red (Pd) and orange (Pt) solids were obtained in good to excellent yields.



Scheme 2.

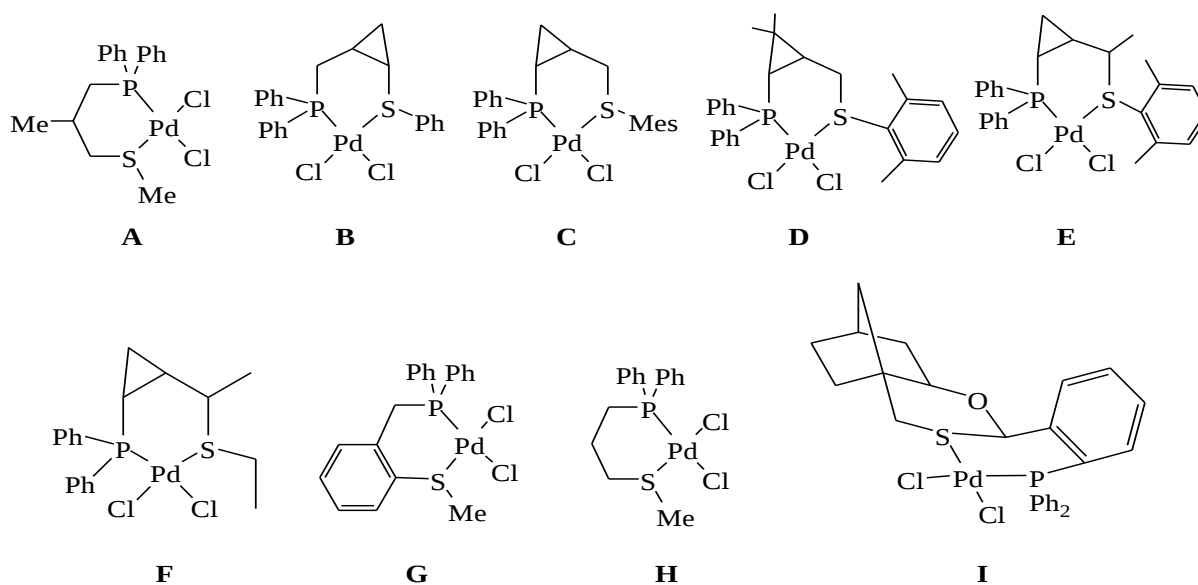
All reactions were carried out with the racemic form of the ligands, thus leading to the products as racemic mixtures. However, the coordination of the thioether function generates a new chiral center on the sulphur atom, thus two distinct diastereoisomers may be obtained in principle. In fact, the reactions are 100% diastereoselective, leading in each case to only one observable product, as shown by NMR spectroscopy. Each product gives one single signal in the ^{31}P NMR spectrum and one set of resonances, notably only one signal for the unsubstituted Cp ring, in the ^1H NMR spectrum. In addition, complexes **3** show the expected satellites corresponding to the Pt-P coupling for the ^{31}P NMR signal. The ^{31}P and ^{195}Pt NMR data are shown in Table 1. The three complexes **2** have analogous ^{31}P chemical shifts (see Table 1) indicating similar structures in solution. In the same way, the four complexes **3** have analogous ^{31}P and ^{195}Pt chemical shifts (see Table 1), leading to the same conclusion. The ^{195}Pt chemical shifts of compounds **3** (from -4030 ppm to -4095 ppm) are in the expected range for such *cis*-Pt(II) complexes and approximately midway relative to complexes containing two P ligands (*cis*-PtCl₂(PMe₃)₂: -4408 ppm) and two S ligands (*cis*-PtCl₂(SMe₂)₂: -3551 ppm) [28]. The Pt-P coupling constant agrees with previously reported values for *cis*-square planar PtCl₂LL' structures containing phosphine-thioether ($J_{\text{P-Pt}} = 3680$ Hz) [29] or diphosphine ($J_{\text{P-Pt}} = 3650$ Hz [29], 3573 Hz [30], 3693 Hz [31], 3810 Hz [32]) ligands.

Table 1. ^{31}P and ^{195}Pt NMR data for compounds **2** and **3**.

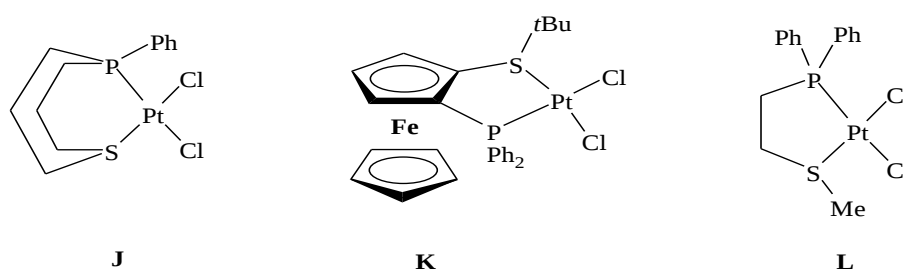
	NMR ^{31}P , $\delta(\text{ppm})$ (CDCl ₃ , 500 MHz)	NMR ^{195}Pt , $\delta(\text{ppm})$ (CDCl ₃ , 500 MHz)	J_{PPt} (Hz)
2a	20.9		
2b	21.2		
2c	22.4		
3a	-0.8	-4093	3608
3b	-3.68	-4110	3666
3c	-3.18	-4030	3636

3d	-0.5	-4095	3660
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Single crystals of each complex **2** and **3** were obtained by slow diffusion of hexane in dichloromethane solutions and used for structural studies by X-ray diffraction. Few other phosphine-thioether-MCl₂ (M = Pd, Pt) complexes have previously been characterized by X-ray diffraction. A few relevant examples for Pd are compounds **A-I** [33-37] in Scheme 3, whereas those of Pt include compounds **J** [38], **K** [39] and **L** [40], shown in Scheme 4. Views of the three Pd structures are shown in Figure 1 (**2a**), Figure 2 (**2b**), Figure 3 (**2c**). The structures of complexes **3a** and **3b** are essentially identical to those of the corresponding Pd complexes. A view of the Pt complexes **3c** and **3d** are shown in Figure 3 and Figure 4, respectively.



Scheme 3.



Scheme 4.

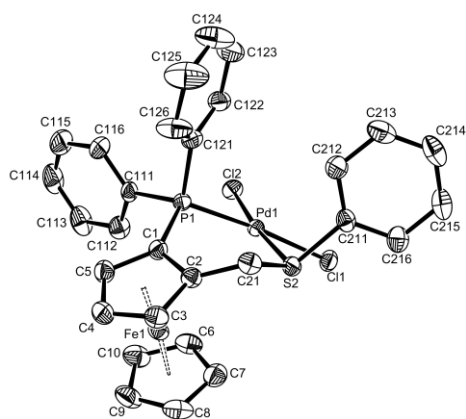


Figure 1. ORTEP view of the palladium complex **2a**.

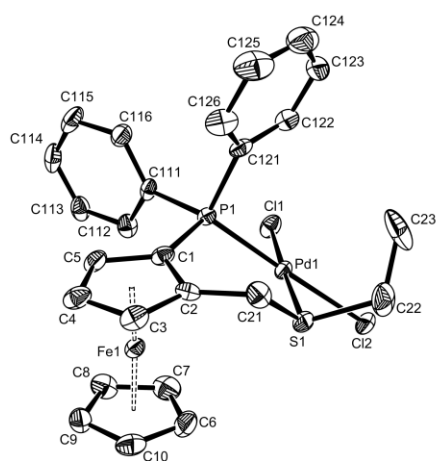


Figure 2. ORTEP view of the palladium complex **2b**.

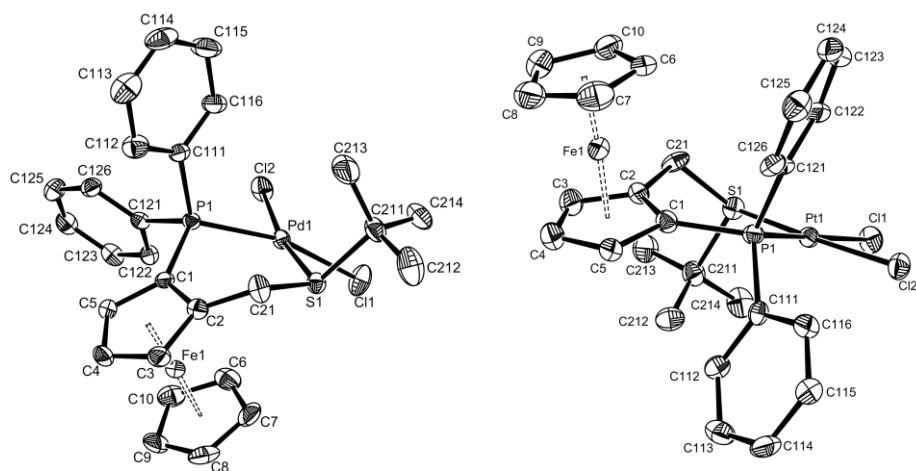


Figure 3. ORTEP view of the palladium complex **2c** and the platinum complex **3c**.

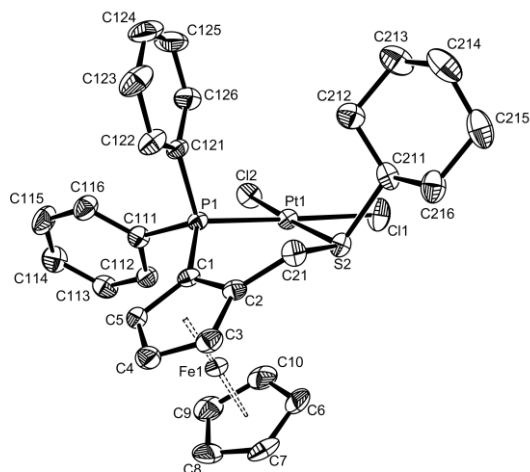


Figure 4. ORTEP view of the platinum complex **3d**.

All compounds adopt a mononuclear square planar geometry with the phosphine and thioether functions in relative *cis* position. In each case, the sulphur substituent is placed opposite (*anti*) to the FeCp group, with respect to the S-C-C-C-P chelate. Thus, the metal atom has been selectively coordinated by one of the two lone pairs of the sulphur atom; after coordination, the remaining lone pair is oriented *syn* to the unsubstituted Cp. Consequently, the observed diastereomer has the configuration (R_P , R_S) or (S_P , S_S) for **2/3a**, **2/3c** and **3d**, and (R_P , S_S) or (S_P , R_S) for **2/3b**. Relevant bond distances and angles for all compounds are compared in Table 2.

Table 2. Selected bond distances (Å) and angles (°) for compounds **2** and **3**.

	M = Pd			M = Pt			
	2a	2b	2c	3a	3b	3c	3d
M-P	2.2311(10)	2.227(2)	2.2251(8)	2.2281(10)	2.2184(12)	2.2395(18)	2.2162(8)
M-S	2.3074(9)	2.308(2)	2.3215(8)	2.2717(11)	2.2826(13)	2.2718(19)	2.2838(8)
M-Cl (<i>t</i> -S)	2.3102(9)	2.313(2)	2.3006(8)	2.3019(11)	2.3173(13)	2.3123(19)	2.3003(8)
M-Cl (<i>t</i> -P)	2.3683(10)	2.365(2)	2.3588(8)	2.3727(11)	2.3694(12)	2.3534(17)	2.3537(8)
P-M-S	95.08(4)	93.90(6)	96.08(3)	95.56(4)	94.71(5)	99.44(7)	95.96(3)
P-M-Cl(<i>c</i>)	90.20(3)	89.80(5)	88.99(3)	90.21(4)	91.03(4)	85.92(7)	90.65(3)

P-M-Cl(<i>t</i>)	175.56(3)	176.50(7)	163.68(3)	176.61(4)	177.32(5)	174.08(7)	178.55(3)
S-M-Cl(<i>c</i>)	83.41(3)	83.75(6)	86.73(3)	84.14(4)	83.71(5)	86.23(7)	84.84(3)
S-M-Cl(<i>t</i>)	173.14(3)	176.28(6)	169.98(3)	173.35(4)	174.24(5)	174.36(6)	173.39(3)
Cl-M-Cl	91.65(4)	92.54(6)	90.82(3)	90.29(4)	90.57(5)	88.37(6)	88.57(3)

In each structure, the M-S bond is longer than the M-P bond, and the M-Cl (*trans* to P) is longer than M-Cl (*trans* to S), in agreement with the stronger *trans*-effect of phosphine donors compared with thioethers. The Pt-P bond is longer in the *t*Bu derivative (**3c**), whereas the Pd-P bond is longer in the Ph derivative (**2a**). On the other hand, the Pt-S bond is longest in the Et complex (**3b**) and the Pd-S bond is longest in the *t*Bu derivative (**2c**). An interpretation of these trends does not appear straightforward. The Pt-P distance in compound **3c** is in fact significantly longer than all those previously reported for this family of compounds (2.208 Å for **J** [38], 2.2209(1) Å for **K** [39], 2.210 Å for **L** [40]), whereas the Pd-P distances for compounds **2** are within the previously established range for compounds **A-I** (2.228-2.237 Å). The Pt-S distances are also within the previously established range (2.256-2.293 Å). On the other hand, all Pd-S distances in compounds **2** are slightly longer than those previously reported for compounds **A-I** (in the 2.257- 2.296 Å range).

The Pd-Cl and Pt-Cl distances are very close to those of the similar compounds already described in the literature. When comparing the related Pd and Pt complexes, the M-Cl distances are essentially identical, whereas the M-P and M-S bonds are generally shorter for the heavier Pt metal (exception made for the M-P bond in **2/3c**). A similar observation was made by Carretero for the platinum complex **K** and for its palladium analogue [39].

The P-M-S angle varies in the same order for both systems (**b** < **a** < **c**), possibly resulting from a growing steric repulsion between the sulphur substituent and the pseudo-axial phosphine Ph group. In the previously reported compounds, this angle spans a range covering the observed values for compounds **2** (90.0-97.8° for **A-I**), whereas it is smaller than the observed values for compounds **3** (87-91° for **J-L**). The angle is smaller for the Pd

complexes with respect to the Pt analogues, as a consequence of the longer Pd-P and Pd-S distances.

It is worth pointing out that the bulky *tert*-butyl substituent on the S atom apparently affects the conformation of the Pt complex. Indeed, upon considering the folding between the two planes defined by the substituted Cp-ring and the square MPSCl₂ plane, the CpFe moiety is placed inside the fold for compounds **2a**, **2b**, **2c**, **3a**, **3b** and **3d** and outside for **3c** (see Figures). This change strongly influences the value of the dihedral angle between the two planes, which is much lower in **3c**, 27.7(1)°, than in the 6 other complex where it ranges from 38.13(6) to 48.21(7)°. The conformation observed in compound **2c** is different than in **3c** and identical to that observed in the other complexes. In this case, the bulky *tert*-butyl group appear to induce a strong deformation of the square plane, with the two Cl atoms being pushed away from the mean plane [by -0.666(3) Å for Cl1 and 0.332(3) Å for Cl2]. The molecular geometry may be considered as lying on the isomerization coordinate leading from square planar to tetrahedral [41].

Conclusion

For the four (P,S) ligands studied, only monomeric Pd(II) or Pt(II) complexes with both P and S atoms coordinated on the same metal in a *cis* geometry were obtained upon reaction with PdCl₂(CH₃CN)₂ or PtCl₂(CH₃CN)₂. For each complex, a slightly distorted square-planar geometry was observed. In addition, only one single diastereoisomer was obtained (both in solution and in solid state) indicating a perfect control of the absolute configuration of the coordinated sulfur atom by the planar chirality of the ferrocene moiety. These observations are of particular interest for the ongoing studies of this type of complexes in asymmetric catalysis.

Experimental section

General.

All reactions were carried out under dry argon by using Schlenk glassware and vacuum line techniques. Solvents were freshly distilled from standard drying agents. ^1H , $^{13}\text{C}\{^1\text{H}$, $^{31}\text{P}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker WMX 400 instrument operating at 400, 162, 100, and 86 MHz respectively. Chemical shifts are reported in parts per million (ppm) relative to Me_4Si (^1H and ^{13}C), 85% H_3PO_4 (^{31}P) or aqueous solution of Na_2PtCl_6 (^{195}Pt). Mass spectra were obtained on a Nermag R10-10 instrument (DCI, FAB) and on a Applied Biosystem API 365 instrument (APCI). Dichlorobis(acetonitrile)palladium(II) and dichlorobis(acetonitrile)platinum(II) were purchased from Strem and used without further purification.

Palladium-dichloro(2-diphenylphosphino-(phenylthiomethyl)ferrocene), 2a. The thioether **1a** (74 mg, 0.15 mmol) and compound $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (39 mg, 0.15 mmol) were dissolved in 10 mL of dry dichloromethane under argon. After stirring for two hours at room temperature, the solvent was evaporated and the resulting red solid was washed with dry pentane. Yield: 88 mg (87%). ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.84 (1H, d, $J_{\text{HP}} = 12$ Hz, PPh_2); 7.83 (1H, d, $J_{\text{HP}} = 12$ Hz, PPh_2); 7.72 (1H, d, $J_{\text{HP}} = 12$ Hz, PPh_2); 7.71 (1H, d, $J_{\text{HP}} = 12$ Hz, PPh_2); 7.61-7.49 (6H, m, Ph); 7.37-7.29 (5H, m, Ph); 4.70 (1H, s large, subst Cp); 4.68 (5H, s, Cp); 4.45 (1H, s large, subst Cp); 4.08 (1H, d(AB), $J_{\text{HH}} = 10$ Hz, $\text{CH}_2\text{-Cp}$); 3.67 (1H, s large, subst Cp); 3.45 (1H, d(AB), $J_{\text{HH}} = 10$ Hz, $\text{CH}_2\text{-Cp}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, CDCl_3) δ (ppm): 134.2 (d, $J_{\text{CP}} = 11$ Hz, m PPh_2); 133.5 (d, $J_{\text{CP}} = 11$ Hz, m PPh_2); 133.3 (s, quat SPh); 132.9 (s, o/m SPh); 132.2 (d, $J_{\text{CP}} = 3$ Hz, p PPh_2); 131.7 (d, $J_{\text{CP}} = 3$ Hz, p PPh_2); 130.5 (s, p SPh); 129.5 (s, m/o SPh); 129.4 (d, $J_{\text{CP}} = 11$ Hz, o PPh_2); 128.5 (d, $J_{\text{CP}} = 51$ Hz, quat PPh_2); 127.9 (d, $J_{\text{CP}} = 12$ Hz, o PPh_2); 127.4 (d, $J_{\text{CP}} = 70$ Hz, quat PPh_2); 84.3 (d, $J_{\text{CP}} = 16$

Hz, quat Cp); 75.3 (d, J_{CP} = 7 Hz, subst Cp); 74.8 (d, J_{CP} = 4 Hz, subst Cp); 71.5 (s, Cp); 69.5 (d, J_{CP} = 7 Hz, subst Cp); 64.6 (d, J_{CP} = 62 Hz, quat Cp); 39.4 (d, J_{CP} = 4 Hz, CH_2 -Cp). ^{31}P NMR (500 MHz, $CDCl_3$) δ (ppm): 20.9 ; MS(DCI; NH_3) : m/z = 688 (M + NH_4 , 28%).

Palladium-dichloro(2-diphenylphosphino-(ethylthiomethyl)ferrocene), 2b. By following the same procedure described in the previous section, the red product was obtained starting from the thioether **1b** (100 mg, 0.225 mmol) and $PdCl_2(CH_3CN)_2$ (58 mg, 0.225 mmol). Yield: 113 mg (81%). 1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.72-7.53 (6H, m, Ph); 7.51-7.41 (4H, m, Ph); 4.63 (5H, s, Cp); 4.56 (1H, s large, subst Cp); 4.41 (1H, s large, subst Cp); 3.78 (1H, d(AB), J_{HH} = 12 Hz, CH_2 -Cp); 3.53 (1H, s large, subst Cp); 3.29 (1H, d, J_{HH} = 12 Hz, CH_2 -Cp); 3.24 (2H, q, J_{HH} = 7 Hz, CH_2 - CH_3); 1.38 (3H, t, J_{HH} = 7 Hz, CH_2 - CH_3). $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$) δ (ppm): 134.1 (d, J_{CP} = 10 Hz, m PPh_2); 133.2 (d, J_{CP} = 11 Hz, m PPh_2); 131.8 (d, J_{CP} = 3 Hz, p PPh_2); 131.6 (d, J_{CP} = 3 Hz, p PPh_2); 129.0 (d, J_{CP} = 11 Hz, o PPh_2); 128.5 (d, J_{CP} = 49 Hz, quat PPh_2); 127.9 (d, J_{CP} = 71 Hz, quat PPh_2); 127.6 (d, J_{CP} = 12 Hz, o PPh_2); 84.4 (d, J_{CP} = 16 Hz, quat Cp); 75.7 (d, J_{CP} = 6 Hz, subst Cp); 74.2 (d, J_{CP} = 4 Hz, subst Cp); 71.4 (s, Cp); 69.3 (d, J_{CP} = 7 Hz, subst Cp); 64.6 (d, J_{CP} = 64 Hz, quat Cp); 35.3 (s, CH_2 - CH_3); 31.5 (d, J_{CP} = 4 Hz, CH_2 -Cp); 13.0 (s, CH_2 - CH_3). ^{31}P NMR (500 MHz, $CDCl_3$) δ (ppm): 21.2. MS(DCI; NH_3) : m/z = 640 (M + NH_4 , 19%).

Palladium-dichloro(2-diphenylphosphino-(tert-butylthiomethyl)ferrocene), 2c. By following the same procedure used for the preparation of **2a**, the red product **2c** was obtained starting from the thioether **1a** (204 mg, 0.43 mmol) and $PdCl_2(CH_3CN)_2$ (112 mg, 0.43 mmol). Yield: 212 mg (77%). 1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.66 (1H, d, J_{HP} = 12 Hz, PPh_2); 7.65 (1H, d, J_{HP} = 13 Hz, PPh_2); 7.62 (1H, d, J_{HP} = 13 Hz, PPh_2); 7.60 (1H, d, J_{HP} = 13 Hz, PPh_2); 7.57-7.46 (4H, m, PPh_2); 7.42 (2H, dt, J_{HH} = 8 Hz, J_{HP} = 3 Hz, PPh_2); 4.74 (5H, s, Cp); 4.71 (1H, s large, subst Cp); 4.42 (1H, s large, subst Cp); 3.78 (1H, d (AB), J_{HH} = 11 Hz, CH_2 -Cp); 3.52 (1H, s large, subst Cp); 3.20 (1H, d(AB), J_{HH} = 12 Hz, CH_2 -Cp), 1.46 (9H,

s, C(CH₃)₃). ¹³C{¹H} NMR (500 MHz, CDCl₃) δ(ppm): 134.0 (d, J_{CP} = 10 Hz, PPh₂); 133.0 (d, J_{CP} = 11 Hz, PPh₂); 132.1 (d, J_{CP} = 3 Hz, p PPh₂); 131.4 (d, J_{CP} = 3 Hz, p PPh₂); 129.3 (d, J_{CP} = 11 Hz, PPh₂); 128.3 (d, J_{CP} = 49 Hz, quat PPh₂); 128.2 (d, J_{CP} = 71 Hz, quat PPh₂); 127.7 (d, J_{CP} = 12 Hz, PPh₂); 84.9 (d, J_{CP} = 17 Hz, quat Cp); 75.3 (d, J_{CP} = 7 Hz, subst Cp); 75.1 (d, J_{CP} = 4 Hz, subst Cp); 71.6 (s, Cp); 69.6 (d, J_{CP} = 7 Hz, subst Cp); 63.7 (d, J_{CP} = 63 Hz, quat Cp); 56.1 (s, C(CH₃)₃); 30.9 (s, C(CH₃)₃); 28.0 (d, J_{CP} = 4 Hz, CH₂-Cp). ³¹P NMR (500 MHz, CDCl₃) δ(ppm): 22.4. MS(DCI; NH₃) : m/z = 668 (M + NH₄, 16 %).

Platinum-dichloro(2-diphenylphosphino-(phenylthiomethyl)ferrocene), 3a. The thioether **1a** (127 mg, 0.258 mmol) and PtCl₂(CH₃CN)₂ (75 mg, 0.216 mmol) were dissolved in 20 mL of dry toluene under argon. After one hour of reflux, the orange solid which formed was filtered and washed with dry pentane, yielding the product as an orange solid (154 mg, 95% yield). ¹H NMR (500 MHz, CDCl₃) δ(ppm): 7.81-7.65 (6H, m, Ph); 7.55-7.40 (6H, m, Ph); 7.41-7.30 (3H, m, Ph); 4.60 (5H, s, Cp); 4.58 (1H, m, subst Cp); 4.38 (1H, td, J_{HH} = 2.5 Hz, J_{HP} = 1 Hz, subst Cp); 4.15 (1H, dd(ABX), J_{HH} = 13 Hz, J_{HP} = 2 Hz, CH₂-Cp); 3.67 (1H, m, subst Cp); 3.61 (1H, d(AB), J_{HH} = 13 Hz, CH₂-Cp). ¹³C{¹H} NMR (500 MHz, CDCl₃) δ(ppm): 134.6 (d, J_{CP} = 11 Hz, m PPh₂); 133.7 (d, J_{CP} = 11 Hz, m PPh₂); 133.3 (s, o SPh); 133.2 (s, quat SPh); 132.1 (d, J_{CP} = 2 Hz, p PPh₂); 132.0 (d, J_{CP} = 2 Hz, p PPh₂); 131.2 (s, p SPh); 129.8 (s, m SPh); 129.5 (d, J_{CP} = 11 Hz, o PPh₂); 129.0 (d, J_{CP} = 60 Hz, quat PPh₂); 128.2 (d, J_{CP} = 12 Hz, o PPh₂); 127.1 (d, J_{CP} = 75 Hz, quat PPh₂); 84.3 (d, J_{CP} = 14 Hz, quat Cp); 75.8 (d, J_{CP} = 7 Hz, subst Cp); 74.6 (d, J_{CP} = 12 Hz, subst Cp); 71.9 (s, Cp); 69.3 (d, J_{CP} = 7 Hz, subst Cp); 65.9 (d, J_{CP} = 73 Hz, quat Cp); 41.5 (d, J_{CP} = 2 Hz, CH₂-Cp). ³¹P NMR (500 MHz, CDCl₃) δ(ppm): -0.8 (satellites ¹⁹⁵Pt : J_{PtP} = 3608 Hz). ¹⁹⁵Pt NMR (500 MHz, CDCl₃) δ(ppm): -4093 (J_{PtP} = 3608 Hz). MS (DCI; NH₃) : m/z = 776 (M + NH₄, 100%).

Platinum-dichloro(2-diphenylphosphino-(ethylthiomethyl)ferrocene), 3b. By following the same procedure described in the previous section, the orange product was

obtained after a 3h reflux starting from the thioether **1b** (350 mg, 0.79 mmol) and $\text{PtCl}_2(\text{CH}_3\text{CN})_2$ (240 mg, 0.70 mmol). Yield; 440 mg (89%). ^1H NMR (500 MHz, CDCl_3) $\delta(\text{ppm})$: 7.72-7.63 (4H, m, Ph); 7.54-7.41 (6H, m, Ph); 4.67 (1H, s large, subst Cp); 4.53 (5H, s, Cp); 4.39 (1H, s large, subst Cp); 3.96 (1H, d(AB), $J_{\text{HH}} = 12$ Hz, $\text{CH}_2\text{-Cp}$); 3.63 (1H, s large, subst Cp); 3.39-3.29 (3H, m, $\text{CH}_2\text{-Cp}$ et $\text{CH}_2\text{-CH}_3$); 1.35 (3H, t, $J_{\text{HH}} = 7$ Hz, $\text{CH}_2\text{-CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, CDCl_3) $\delta(\text{ppm})$: 134.2 (d, $J_{\text{CP}} = 11$ Hz, m PPh_2); 133.3 ($J_{\text{CP}} = 11$ Hz, m PPh_2); 131.6 (d, $J_{\text{CP}} = 2$ Hz, p PPh_2); 131.5 (d, $J_{\text{CP}} = 2$ Hz, p PPh_2); 128.9 (d, $J_{\text{CP}} = 11$ Hz, o PPh_2); 128.5 (d, $J_{\text{CP}} = 62$ Hz, quat PPh_2); 127.7 (d, $J_{\text{CP}} = 11$ Hz, o PPh_2); 126.8 (d, $J_{\text{CP}} = 76$ Hz, quat PPh_2); 84.3 (d, $J_{\text{CP}} = 15\text{Hz}$, quat Cp); 75.3 (d, $J_{\text{CP}} = 7$ Hz, subst Cp); 73.9 (d, $J_{\text{CP}} = 5\text{Hz}$, subst Cp); 71.4 (s, Cp); 68.8 (d, $J_{\text{CP}} = 8$ Hz, subst Cp); 65.8 (d, $J_{\text{CP}} = 73$ Hz, quat Cp); 35.5 (s, $\text{CH}_2\text{-CH}_3$); 31.5 (d, $J_{\text{CP}} = 3$ Hz, $\text{CH}_2\text{-Cp}$); 13.7 (s, $\text{CH}_2\text{-CH}_3$). ^{31}P NMR (500 MHz, CDCl_3) $\delta(\text{ppm})$: -3.68 (satellites ^{195}Pt : $J_{\text{PtP}} = 3666$ Hz). ^{195}Pt NMR (500 MHz, CDCl_3) $\delta(\text{ppm})$: -4110 ($J_{\text{PtP}} = 3666$ Hz). MS(DCI; NH_3) : $m/z = 728$ ($\text{M} + \text{NH}_4$, 100%).

Platinum-dichloro(2-diphenylphosphino-(*tert*-butylthiomethyl)ferrocene), 3c. By following the same procedure used for the preparation of **3a**, the orange product **3c** was obtained after a 3h reflux starting from the thioether **1c** (370 mg, 0.78 mmol) and $\text{PtCl}_2(\text{CH}_3\text{CN})_2$ (240 mg, 0.70 mmol). Yield: 480 mg (93%). ^1H NMR (500 MHz, CDCl_3) $\delta(\text{ppm})$: 7.69 (1H, d, $J_{\text{HP}} = 13$ Hz, m PPh_2); 7.67 (1H, d, $J_{\text{HP}} = 13$ Hz, m PPh_2); 7.59 (1H, d, $J_{\text{HP}} = 13$ Hz, m PPh_2); 7.57 (1H, d, $J_{\text{HP}} = 13$ Hz, m PPh_2); 7.53-7.50 (2H, m, PPh_2); 7.46-7.43 (4H, m, PPh_2); 4.63 (1H, s large, subst Cp); 4.56 (5H, s, Cp); 4.38 (1H, s large, subst Cp); 3.99 (1H, d(AB), $J_{\text{HH}} = 13$ Hz, $\text{CH}_2\text{-Cp}$); 3.66 (1H, s large, subst Cp); 3.39 (1H, d(AB), $J_{\text{HH}} = 13$ Hz, $\text{CH}_2\text{-Cp}$); 1.42 (9H, s, $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, CDCl_3) $\delta(\text{ppm})$: 134.1 (d, $J_{\text{CP}} = 11$ Hz, m PPh_2); 133.2 (d, $J_{\text{CP}} = 11$ Hz, m PPh_2); 131.6 (d, $J_{\text{CP}} = 3$ Hz, p PPh_2); 131.3 (d, $J_{\text{CP}} = 3$ Hz, p PPh_2); 128.9 (d, $J_{\text{CP}} = 11$ Hz, o PPh_2); 128.5 (d, $J_{\text{CP}} = 60$ Hz, quat PPh_2); 127.7 (d, $J_{\text{CP}} = 76$ Hz, quat PPh_2); 127.6 (d, $J_{\text{CP}} = 12$ Hz, o PPh_2); 84.5 (d, $J_{\text{CP}} = 15\text{Hz}$, quat Cp);

74.7 (d, $J_{CP} = 8$ Hz, subst Cp); 74.6 (d, $J_{CP} = 7$ Hz, subst Cp); 71.5 (s, Cp); 68.6 (d, $J_{CP} = 8$ Hz, subst Cp); 65.6 (d, $J_{CP} = 72$ Hz, quat Cp); 56.3 (s, $\underline{C}(\text{CH}_3)_3$); 30.5 (s, $\text{C}(\underline{\text{C}}\text{H}_3)_3$); 29.5 (d, $J_{CP} = 3$ Hz, $\underline{\text{C}}\text{H}_2\text{-Cp}$); ^{31}P NMR (500 MHz, CDCl_3) $\delta(\text{ppm})$: -3.18 (satellites ^{195}Pt : $J_{\text{PPt}} = 3636$ Hz). ^{195}Pt NMR (500 MHz, CDCl_3) $\delta(\text{ppm})$: -4030 ($J_{\text{PPt}} = 3636$ Hz) ; MS(DCI; NH_3) : $m/z = 756(\text{M} + \text{NH}_4, 26\%)$.

Platinum-dichloro(2-diphenylphosphino-cyclohexylthiomethyl)ferrocene), 3d. By following the same procedure used for the preparation of **3a**, the orange product **3d** was obtained after a 1h reflux starting from the thioether **1d** (95 mg, 0.191 mmol) and $\text{PtCl}_2(\text{CH}_3\text{CN})_2$ (56 mg, 0.173 mmol). Yield: 123 mg (93%). ^1H NMR (500 MHz, CDCl_3) $\delta(\text{ppm})$: 7.7-7.45 (10H, m : PPh_2); 4.66 (1H, m : subst Cp); 4.57 (5H, s : Cp); 4.41 (1H, td, $J_{\text{HH}} = 2.5\text{Hz}$ and $J_{\text{PH}} = 0.9\text{Hz}$: subst Cp); 3.94 (1H, m : CH); 3.80 (1H, dd (ABX), $J_{\text{HH}} = 12.6\text{Hz}$ and $J_{\text{PH}} = 1.8\text{Hz}$: $\underline{\text{C}}\text{H}_2\text{Cp}$); 3.63 (1H, m : subst Cp); 3.30 (1H, d (AB), $J_{\text{HH}} = 12.6\text{Hz}$: $\underline{\text{C}}\text{H}_2\text{Cp}$); 2.50 (1H, m : Cy); 2.15 (1H, m : Cy); 1.85-1.05 (8H, m : Cy). $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, CDCl_3) $\delta(\text{ppm})$: 134.3 (d, $J_{CP} = 10.8\text{Hz}$: PPh_2); 133.7 (d, $J_{CP} = 11.0\text{Hz}$: PPh_2); 131.9 (d, $J_{CP} = 3.9\text{Hz}$: PPh_2); 131.7 (d, $J_{CP} = 4.0\text{Hz}$: PPh_2); 129.2 (d, $J_{CP} = 11.2\text{Hz}$: PPh_2); 128.6 (d, $J_{CP} = 61.9\text{Hz}$: quat PPh_2) ; 128.0 (d, $J_{CP} = 12.1\text{Hz}$: PPh_2); 127.4 (d, $J_{CP} = 75.3\text{Hz}$: quat PPh_2) ; 84.6 (d, $J_{CP} = 14.7\text{Hz}$: quat Cp); 75.8 (d, $J_{CP} = 7.1\text{Hz}$: subst Cp); 74.5 (d, $J_{CP} = 5.4\text{Hz}$: subst Cp); 71.7 (s : Cp); 69.1 (d, $J_{CP} = 7.5\text{Hz}$: subst Cp); 65.9 (d, $J_{CP} = 73.5\text{Hz}$: quat Cp); 52.8 (s : CH); 32.1 (s : Cy); 31.8 (s : Cy); 27.4 (s : Cy); 27.0 (s : Cy); 26.2 (s : $\underline{\text{C}}\text{H}_2\text{Cp}$); 25.5 (s : Cy). ^{31}P NMR (500 MHz, CDCl_3) $\delta(\text{ppm})$: -0.5 (satellites ^{195}Pt : $J_{\text{PPt}} = 3660\text{Hz}$). ^{195}Pt NMR (500 MHz, CDCl_3) $\delta(\text{ppm})$: -4095 (d, $J_{\text{PPt}} = 3660\text{Hz}$).

X-ray crystallography. A single crystal of each compound was mounted under inert perfluoropolyether at the tip of a glass fibre and cooled in the cryostream of either an Oxford-Diffraction XCALIBUR CCD or a Stoe IPDS diffractometer. Data were collected using the monochromatic $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$).

The structures were solved by direct methods (SIR97) [42] and refined by least-squares procedures on F^2 using SHELXL-97 [43]. All H atoms attached to carbon were introduced in idealised positions and treated as riding models in the calculations. In compound **2b**, there are two molecules within the asymmetric unit and surprisingly they have opposite planar chirality (*R* and *S*) even though they are not related by any symmetry elements; the Flack's parameter [44] close to 0 is indicative of a non centrosymmetric structure. The drawing of the molecules was realised with the help of ORTEP3 [45]. Crystal data and refinement parameters are shown in .

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 653929 - 653935. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Table 3. Crystal data and structure refinement for all compounds.

Identification code	2a	2b	2b	2c	3a	3b	3c	3d
Empirical formula	C ₃₀ H ₂₆ Cl ₅ FePPdS	C ₂₅ H ₂₅ Cl ₂ FePPdS	C ₂₅ H ₂₅ Cl ₂ FePPdS	C ₂₇ H ₂₉ Cl ₂ FePPdS	C ₃₀ H ₂₆ Cl ₅ FePPtS	C ₂₅ H ₂₅ Cl ₂ FePPtS	C ₂₇ H ₂₉ Cl ₂ FePPtS	C ₂₉ H ₃₁ Cl ₂ FePPtS
Formula weight	789.04	621.63	621.63	649.68	877.73	710.32	738.37	764.41
Temperature, K	180(2) K	180(2)	180(2)	180(2)	180(2)	180(2)	180(2)	180(2)
Wavelength, Å	0.71073 Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P 2 ₁ /c	C c	P 1	P 2 ₁ /c	P 2 ₁ /c	C c	P2 ₁ /n	P 2 ₁ /c
a, Å	9.5438(10)	8.7773(12)	8.7773(12)	14.9597(11)	9.8065(8)	8.7912(6)	16.6696(12)	16.9666(16)
b, Å	33.331(3)	23.879(4)	11.6335(16)	7.9180(6)	28.039(3)	24.0504(15)	9.3976(9)	7.9977(5)
c, Å	10.4509(10)	11.6335(16)	12.7214(17)	21.5814(14)	12.0321(10)	11.6258(8)	17.8129(12)	21.794(2)
α, °	90.0	90.0	86.165(11)	90.0	90.0	90.0	90.0	90.0
β, °	110.756(11)	100.872(12)	69.805(13)	96.274(6)	109.565(10)	100.631(6)	114.504(7)	112.454(11)
γ, °	90.0	90.0	79.128(12)	90.0	90.0	90.0	90.0	90.0
V, Å ³	3108.7(5)	2394.5(6)	1197.2(3)	2541.0(3)	3117.4(5)	2415.9(3)	2539.1(3)	2733.1(4)
Z	4	4	2	4	4	4	4	4
D _x , Mg/m ³	1.686	1.724	1.724	1.698	1.870	1.953	1.932	1.858
μ, mm ⁻¹	1.614	1.746	1.746	1.649	5.515	6.770	6.446	5.992
F(000)	1576	1248	624	1312	1704	1376	1440	1496
Crystal size, mm ³	0.32x0.12x0.08	0.237x0.204x0.097	0.237x0.204x0.097	0.48 x 0.4 x 0.09	0.32x0.16x0.14	0.23x0.184x0.177	0.1x0.06x0.03	0.32x0.1x0.1
θ range, °	2.28 - 24.16	3.33 - 28.28	3.33 - 28.28	2.74 - 28.22	2.20 - 26.03	2.81 - 28.27	2.51 - 26.09	2.74 - 25.98
Reflns, collected	19490	12684	10609	20310	29524	9942	19951	21184
Reflns, unique [R(int)]	4868 [0.0333]	5837 [0.0608]	7575 [0.0443]	6300 [0.0349]	5804 [0.0387]	4870 [0.0186]	4744 [0.0728]	5307 [0.0315]
Completeness, %	98.3	93.6	99.3	99.8	94.6	99.8	94.2	99.2
Absorption correction	Multiscan	Multiscan	Multiscan	Multiscan	Multiscan	Multiscan	Empirical	Multiscan
Max., min. transm.	0.7738, 0.7275	0.8028, 0.6749	0.8028, 0.6749	0.7510, 0.4512	0.3858, 0.2107	0.3041, 0.2364	0.8240, 0.4611	0.4652, 0.3792
Refinement	F ²	F ²	F ²	F ²	F ²	F ²	F ²	F ²
Data/restraints/param.	4868 / 0 / 352	5837 / 2 / 281	7575 / 3 / 562	6300 / 0 / 301	5804 / 0 / 391	4870 / 2 / 282	4744 / 0 / 301	5307 / 0 / 316
GOF on F ²	1.013	0.969	0.984	1.041	1.104	1.149	0.928	1.021
R, wR2 [I>2σ(I)]	0.0310, 0.0762	0.0468, 0.1022	0.0475, 0.1061	0.0340, 0.0853	0.0285, 0.0717	0.0183, 0.0420	0.0360, 0.0713	0.0208, 0.0459
R, wR2 (all data)	0.0403, 0.0797	0.0640, 0.1105	0.0600, 0.1122	0.0463, 0.0963	0.0338, 0.0825	0.0199, 0.0541	0.0640, 0.0786	0.0267, 0.0473
Flack's parameter		0.02(3)	0.06(4)			-0.008(5)		
(Max/ min)Δe, e.Å ⁻³	1.318 / -1.000	1.659 / -1.677	1.252 / -1.324	0.928 / -0.90	1.204 / -1.891	1.724 / -1.230	1.107 / -0.894	1.169 / -0.992