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Conversion of $[Pt(SRf)_2(PPh_{2-n}(C_6F_5)_{n+1})_2]$ (n = 0 or 1, Rf=C_6HF_4-4) through carbon–fluorine bond activation to $[Pt(SRf)_2(1,2\text{-}C_6F_4(SRf)\text{-}(PPh_2))]$ and chiral $[Pt(SRf)_2(1,2\text{-}C_6F_4(SRf)(PPh(C_6F_5)))]$†

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Treatment of *trans*-$[PtCl_2(PPh_{2-n}(C_6F_5)_{n+1})_2]$ (n = 0 or 1) with $Pb(SC_6HF_4\text{-}4)_2$ yields a mixture of monometallic *cis*/*trans* $[Pt(SC_6HF_4\text{-}4)_2(PPh_{2-n}(C_6F_5)_{n+1})_2]$, thiolate-bridged bimetallic *cis*/*trans* $[Pt_2(\mu\text{-}SC_6HF_4\text{-}4)_2(SC_6HF_4\text{-}4)_2(PPh_{2-n}(C_6F_5)_{n+1})_2]$ and $[Pt(SC_6HF_4\text{-}4)_2(1,2\text{-}C_6F_4(SC_6HF_4\text{-}4)(PPh_{2-n}(C_6F_5)_n)]$.

The metal assisted functionalization of fluorinated hydrocarbons has been an area of intense study during the last decade. Several reports of carbon–fluorine bond activation have been published[1] and there are also a number of structural determinations of transition metal complexes with C–F→M interactions.[2] The subject has been reviewed.[3]

Previously, we have reported the synthesis of $[M(SC_6F_5)_3(PMe_2Ph)_2]$ (M = Ru, Os), showing by X-ray diffraction that both compounds bear a C–F→M interaction in the solid state.[4] Following this interest, we have extended our work to include fluorinated phosphine containing platinum complexes. Although platinum derivatives of fluorinated phosphines are well know, very few examples of carbon–fluorine bond activation at platinum centres are known[5,6] and none of these studies include fluorothio-substituents.

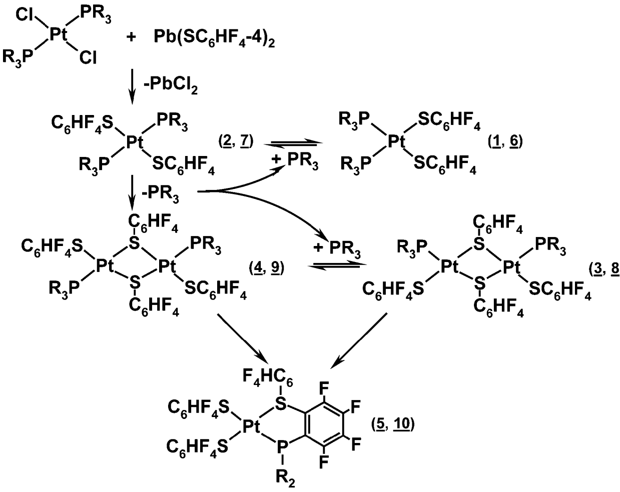
Treatment of *trans*-$[PtCl_2(PPh_2(C_6F_5))_2]$ with $Pb(SC_6HF_4\text{-}4)_2$ in acetone at room temperature yields a complex equilibrium mixture of monometallic *cis* and *trans* $[Pt(SC_6HF_4\text{-}4)_2(PPh_2(C_6F_5))_2]$ (*cis* **1**, *trans* **2**), thiolate bridged bimetallic *cis* and *trans* $[Pt_2(\mu\text{-}SC_6HF_4\text{-}4)_2(SC_6HF_4\text{-}4)_2(PPh_2(C_6F_5))_2]$ (*cis* **3**, *trans* **4**) and $[Pt(SC_6HF_4\text{-}4)_2(1,2\text{-}C_6F_4(SC_6HF_4\text{-}4)(PPh_2))]$ **5**, which can be isolated as yellow diamagnetic crystalline solids. A similar reaction with *trans*-$[PtCl_2(PPh(C_6F_5)_2)_2]$ affords *cis* and *trans* $[Pt(SC_6HF_4\text{-}4)_2(PPh(C_6F_5)_2)_2]$ (*cis* **6**, *trans* **7**), *cis* and *trans* $[Pt_2(\mu\text{-}SC_6HF_4\text{-}4)_2(SC_6HF_4\text{-}4)_2(PPh(C_6F_5)_2)_2]$ (*cis* **8**, *trans* **9**) and the chiral complex $[Pt(SC_6HF_4\text{-}4)_2(1,2\text{-}C_6F_4(SC_6HF_4\text{-}4)(PPh\text{–}(C_6F_5))]$ **10**. Both reactions also freed the corresponding fluorophosphine ligand.

On standing as acetone solutions at room temperature, none of the pure complexes *trans*-$[Pt(SC_6HF_4\text{-}4)_2(PPh_2(C_6F_5))_2]$ **2** or *trans*-$[Pt(SC_6HF_4\text{-}4)_2(PPh(C_6F_5)_2)_2]$ **7** give rise to the related *cis* isomer unless the corresponding free phosphine is present in the reaction medium. Therefore, formation of the thiolate bridged bimetallic compounds probably stems from compounds **2** and **7**, a reaction that liberates the fluorophosphine which, in turn, promotes the *cis*–*trans* isomerization, affording compounds **1** and **6** as shown in Scheme 1.

Examples of both, *cis* and *trans* monometallic fluorophosphines containing Pt(II) complexes have been structurally characterized previously[7] but, to our knowledge, no member of the thiolate-bridged family with fluorophosphines has been structurally studied before. The molecular structure of **8** is shown in Fig. 1.‡

As above, on standing as acetone solutions at room temperature, neither pure *cis* or *trans* $[Pt_2(\mu\text{-}SC_6HF_4\text{-}4)_2(SC_6HF_4\text{-}4)_2(PPh_2(C_6F_5))_2]$ (**3**, **4**) nor *cis* or *trans* $[Pt_2(\mu\text{-}SC_6HF_4\text{-}4)_2(SC_6HF_4\text{-}4)_2(PPh(C_6F_5)_2)_2]$ (**8**, **9**) transform into each other unless the corresponding free phosphine is present in the reaction medium.

$[Pt_2(\mu\text{-}SC_6HF_4\text{-}4)_2(SC_6HF_4\text{-}4)_2(PPh_2(C_6F_5))_2]$ and $[Pt_2(\mu\text{-}SC_6HF_4\text{-}4)_2(SC_6HF_4\text{-}4)_2(PPh(C_6F_5)_2)_2]$ evolve with intramolecular formation of the new ligands 2-(4-tetrafluorophenylthio)-3,4,5,6-tetrafluorophenyldiphenylphosphine and 2-(4-tetrafluorophenylthio)-3,4,5,6-tetrafluorophenylphenylpentafluorophenylphosphine giving rise to the complexes $[Pt(SC_6HF_4\text{-}4)_2(1,2\text{-}C_6F_4\text{-}$



Scheme 1 R_2 = Ph_2 or $Ph(C_6F_5)$, R_3 = $Ph_2(C_6F_5)$ or $Ph(C_6F_5)_2$.

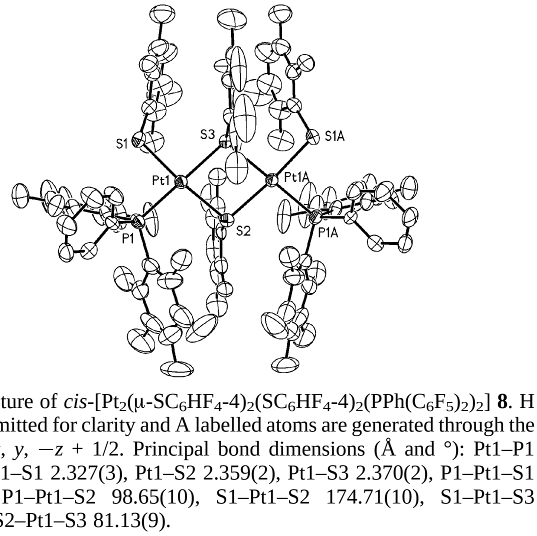


Fig. 1 Structure of *cis*-$[Pt_2(\mu\text{-}SC_6HF_4\text{-}4)_2(SC_6HF_4\text{-}4)_2(PPh(C_6F_5)_2)_2]$ **8**. H atoms are omitted for clarity and A labelled atoms are generated through the symmetry $x, y, -z + 1/2$. Principal bond dimensions (Å and °): Pt1–P1 2.268(3), Pt1–S1 2.327(3), Pt1–S2 2.359(2), Pt1–S3 2.370(2), P1–Pt1–S1 86.44(11), P1–Pt1–S2 98.65(10), S1–Pt1–S2 174.71(10), S1–Pt1–S3 93.83(10), S2–Pt1–S3 81.13(9).

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† Electronic Supplementary Information (ESI) available: experimental procedures and spectral data for all new compounds and crystallographic data for **5**, **8** and **10**. http://www.rsc.org/suppdata/cc/b4/b407328b/

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$(SC_6HF_4\text{-}4)(PPh_2))]$ **5** and a racemic mixture of $[Pt(SC_6HF_4\text{-}4)_2(1,2\text{-}C_6F_4(SC_6HF_4)(PPh(C_6F_5))]$ **10** which have been structurally characterized as shown in Figs. 2 and 3. For **10** a racemic mixture was crystallized.

Although the ligands $1,2\text{-}C_6F_4(SMe)(PPh_2)$, $(1,2\text{-}C_6F_4\text{–}(SMe))_2(PPh)$ and $1,2\text{-}C_6H_4(SMe)(P(C_6F_5)2)$ are known,[8] complexes **5** and **10** are rare examples of metal promoted C–F activation from $PPh_{3-n}(C_6F_5)_n$ (n = 1 or 2) involving polyfluorothiolate ligands to afford 1-thiolate-2-phosphine–tetrafluorophenyl complexes.

Unfortunately, to date we have been unable to detect the freed fluorine atom or any other fluorine containing species using either mass spectrometry or ^{19}F NMR (Pt–F, $-200 < \delta < -300$ ppm).[9]

To rationalize the outcome from these reactions, activation and cleavage of an *ortho* carbon–fluorine bond at a phosphine ligand, transfer of a thiolate moiety and rearrangement of the parent bimetallic complexes have to be considered. A related reaction[6] is the formation of the oxocarboplatinum $[PtMe(2\text{-}OC_6F_4PPh_2)(PPh_2(C_6F_5))]$ from moist $[PtMe(THF)(PPh_2\text{–}(C_6F_5))_2]$. An Ar–F→Pt interaction is expected to induce an activated *ortho*-C–F bond bearing an electrophilic carbon atom. Such interactions are known to render C–F bonds highly susceptible to nucleophilic attack.[3] Therefore the *ortho*-carbon atoms C1 of complexes **5** and **10**—Figs. 2 and 3—can be envisaged as the centres of a nucleophilic attack by a thiolate-sulfur atom. Nucleophilic displacement of *ortho*-fluorine from polyfluorinated aromatic ligands attached to transition metals has been observed in a few examples where the C_6F_5 ring is bound to carbon or phosphorus atoms.[3]

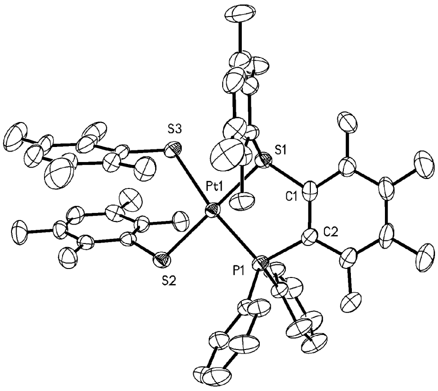

Fig. 2 Structure of $[Pt(SC_6HF_4\text{-}4)_2(1,2\text{-}C_6F_4(SC_6HF_4\text{-}4)(PPh_2))]$ **5**. H atoms are omitted for clarity. Principal bond dimensions (Å and °): Pt1–P1 2.261(2), Pt1–S1 2.268(2), Pt1–S2 2.300(2), Pt1–S3 2.378(2), S1–Pt1–P1 89.91(8), S2–Pt1–S3 97.65(8).

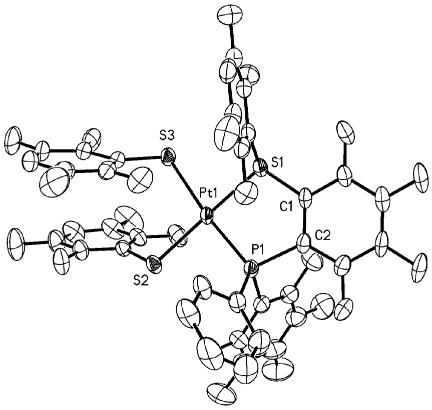

Fig. 3 Structure of $[Pt(SC_6HF_4\text{-}4)_2(1,2\text{-}C_6F_4(SC_6HF_4\text{-}4)(PPh(C_6F_5))]$ **10**. H atoms are omitted for clarity. Principal bond dimensions (Å and °): Pt1–P1 2.2313(14), Pt1–S1 2.2812(14), Pt1–S2 2.3064(15), Pt1–S3 2.3537(14), S1–Pt1–P1 89.41(5), S2–Pt1–P3 96.74(5).

Notes and references

‡ *Crystal data*. Bruker P4 diffractometer, Mo–K_α (λ = 0.71073 Å), operated at room temp. **8**: $C_{60}H_{14}F_{36}P_2Pt_2S_4$, MW = 1999.07, hexagonal, $P6_3/m$, $a = b = 25.675(2)$, $c = 19.115(2)$, $Z = 6$, $D_{calcd} = 1.825$ g cm^{-3}. $R1 = 0.0542$ for 3631 $I > 2\sigma(I)$ and $wR = 0.1528$ for 6577 data, 502 parameters and 28 restraints. **5**: $C_{36}H_{13}F_{16}PPtS_3$, MW = 1071.70, triclinic, $P\bar{1}$, $a = 11.945(3)$, $b = 12.0754(14)$, $c = 13.4898(18)$, $\alpha = 102.108(10)$, $\beta = 102.397(17)$, $\gamma = 105.499(14)$, $Z = 2$, $D_{calcd} = 2.027$ g cm^{-3}. $R1 = 0.0431$ for 4627 $I > 2\sigma(I)$ and $wR = 0.1023$ for 6109 data and 514 parameters. **10**: $C_{36}H_8F_{21}PPtS_3$, MW = 1161.66, triclinic, $P\bar{1}$, $a = 11.8338(10)$, $b = 12.4575(14)$, $c = 14.5848(13)$, $\alpha = 96.898(8)$, $\beta = 107.898(7)$, $\gamma = 105.595(7)$, $Z = 2$, $D_{calcd} = 2.007$ g cm^{-3}. $R1 = 0.0348$ for 5688 $I > 2\sigma(I)$ and $wR = 0.0849$ for 6727 data and 559 parameters. CCDC 239571–239573. See http://www.rsc.org/suppdata/cc/b4/b407328b/ for crystallographic data in .cif or other electronic format.

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