

Conversion of $[\text{Pt}(\text{SRf})_2(\text{PPh}_2 - n(\text{C}_6\text{F}_5)_{n+1})_2]$ ($n = 0$ or 1 , $\text{Rf} = \text{C}_6\text{HF}_4-4$) through carbon–fluorine bond activation to $[\text{Pt}(\text{SRf})_2(1,2-\text{C}_6\text{F}_4(\text{SRf})-(\text{PPh}_2))]$ and chiral $[\text{Pt}(\text{SRf})_2(1,2-\text{C}_6\text{F}_4(\text{SRf})(\text{PPh}(\text{C}_6\text{F}_5)))]$ †

Luis Villanueva,^a Maribel Arroyo,^b Sylvain Bernès^b and Hugo Torrens^{*a}

^a Facultad de Química, UNAM, Cd. Universitaria, 04510 México D.F., Mexico.

E-mail: torrens@servidor.unam.mx

^b Centro de Química, Instituto de Ciencias, Benemerita Universidad Autónoma de Puebla, Blvd. 14 Sur 6303, San Manuel, 72570 Puebla, Puebla, Mexico

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Treatment of *trans*- $[\text{PtCl}_2(\text{PPh}_2 - n(\text{C}_6\text{F}_5)_{n+1})_2]$ ($n = 0$ or 1) with $\text{Pb}(\text{SC}_6\text{HF}_4)_2$ yields a mixture of monometallic *cis/trans* $[\text{Pt}(\text{SC}_6\text{HF}_4)_2(\text{PPh}_2 - n(\text{C}_6\text{F}_5)_{n+1})_2]$, thiolate-bridged bimetallic *cis/trans* $[\text{Pt}_2(\mu-\text{SC}_6\text{HF}_4)_2(\text{SC}_6\text{HF}_4)_2(\text{PPh}_2 - n(\text{C}_6\text{F}_5)_{n+1})_2]$ and $[\text{Pt}(\text{SC}_6\text{HF}_4)_2(1,2-\text{C}_6\text{F}_4(\text{SC}_6\text{HF}_4)-(\text{PPh}_2 - n(\text{C}_6\text{F}_5)_n))]$.

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 published¹ 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 $[\text{M}(\text{SC}_6\text{F}_5)_3(\text{PMe}_2\text{Ph})_2]$ ($\text{M} = \text{Ru}, \text{Os}$), 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 known, 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*- $[\text{PtCl}_2(\text{PPh}_2(\text{C}_6\text{F}_5)_2)_2]$ with $\text{Pb}(\text{SC}_6\text{HF}_4)_2$ in acetone at room temperature yields a complex equilibrium mixture of monometallic *cis* and *trans* $[\text{Pt}(\text{SC}_6\text{HF}_4)_2(\text{PPh}_2(\text{C}_6\text{F}_5)_2)_2]$ (*cis* **1**, *trans* **2**), thiolate bridged bimetallic *cis* and *trans* $[\text{Pt}_2(\mu-\text{SC}_6\text{HF}_4)_2(\text{SC}_6\text{HF}_4)_2(\text{PPh}_2(\text{C}_6\text{F}_5)_2)_2]$ (*cis* **3**, *trans* **4**) and $[\text{Pt}(\text{SC}_6\text{HF}_4)_2(1,2-\text{C}_6\text{F}_4(\text{SC}_6\text{HF}_4)-(\text{PPh}_2))]$ **5**, which can be isolated as yellow diamagnetic crystalline solids. A similar reaction with *trans*- $[\text{PtCl}_2(\text{PPh}(\text{C}_6\text{F}_5)_2)_2]$ affords *cis* and *trans* $[\text{Pt}(\text{SC}_6\text{HF}_4)_2(\text{PPh}(\text{C}_6\text{F}_5)_2)_2]$ (*cis* **6**, *trans* **7**), *cis* and *trans* $[\text{Pt}_2(\mu-\text{SC}_6\text{HF}_4)_2(\text{SC}_6\text{HF}_4)_2(\text{PPh}(\text{C}_6\text{F}_5)_2)_2]$ (*cis* **8**, *trans* **9**) and the chiral complex $[\text{Pt}(\text{SC}_6\text{HF}_4)_2(1,2-\text{C}_6\text{F}_4(\text{SC}_6\text{HF}_4)-(\text{PPh}-(\text{C}_6\text{F}_5)))]$ **10**. Both reactions also freed the corresponding fluorophosphine ligand.

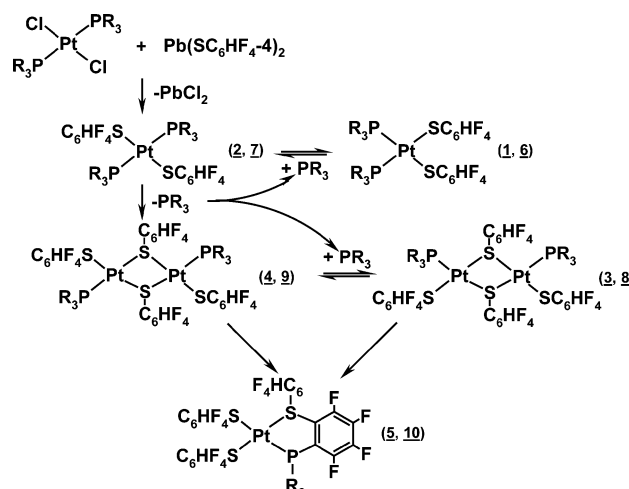
On standing as acetone solutions at room temperature, none of the pure complexes *trans*- $[\text{Pt}(\text{SC}_6\text{HF}_4)_2(\text{PPh}_2(\text{C}_6\text{F}_5)_2)_2]$ **2** or *trans*- $[\text{Pt}(\text{SC}_6\text{HF}_4)_2(\text{PPh}(\text{C}_6\text{F}_5)_2)_2]$ **7** give rise to the related *cis* 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 previously⁷ 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.†

† 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/>

As above, on standing as acetone solutions at room temperature, neither pure *cis* or *trans* $[\text{Pt}_2(\mu-\text{SC}_6\text{HF}_4)_2(\text{SC}_6\text{HF}_4)_2(\text{PPh}_2(\text{C}_6\text{F}_5)_2)_2]$ (**3**, **4**) nor *cis* or *trans* $[\text{Pt}_2(\mu-\text{SC}_6\text{HF}_4)_2(\text{SC}_6\text{HF}_4)_2(\text{PPh}(\text{C}_6\text{F}_5)_2)_2]$ (**8**, **9**) transform into each other unless the corresponding free phosphine is present in the reaction medium.

$[\text{Pt}_2(\mu-\text{SC}_6\text{HF}_4)_2(\text{SC}_6\text{HF}_4)_2(\text{PPh}_2(\text{C}_6\text{F}_5)_2)_2]$ and $[\text{Pt}_2(\mu-\text{SC}_6\text{HF}_4)_2(\text{SC}_6\text{HF}_4)_2(\text{PPh}(\text{C}_6\text{F}_5)_2)_2]$ 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 $[\text{Pt}(\text{SC}_6\text{HF}_4)_2(1,2-\text{C}_6\text{F}_4-$



Scheme 1 $\text{R}_2 = \text{Ph}_2$ or $\text{Ph}(\text{C}_6\text{F}_5)$, $\text{R}_3 = \text{Ph}_2(\text{C}_6\text{F}_5)$ or $\text{Ph}(\text{C}_6\text{F}_5)_2$.

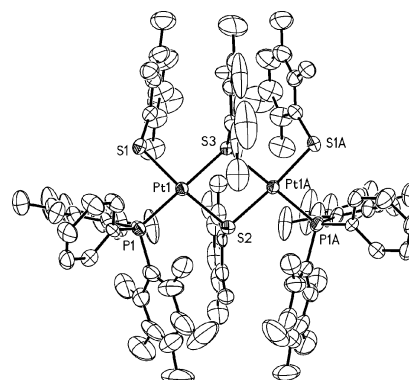


Fig. 1 Structure of *cis*- $[\text{Pt}_2(\mu-\text{SC}_6\text{HF}_4)_2(\text{SC}_6\text{HF}_4)_2(\text{PPh}(\text{C}_6\text{F}_5)_2)_2]$ **8**. H atoms are omitted for clarity and A labelled atoms are generated through the symmetry $x, y, -z + 1/2$. Principal bond dimensions (Å and °): Pt1–P1 2.268(3), 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).

(SC₆HF₄-4)(PPh₂)] **5** and a racemic mixture of [Pt(SC₆HF₄-4)₂(1,2-C₆F₄(SC₆HF₄)(PPh(C₆F₅))] **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-C₆F₄(SMe)(PPh₂), (1,2-C₆F₄(SMe))₂(PPh) and 1,2-C₆F₄(SMe)(P(C₆F₅)₂) are known,⁸ complexes **5** and **10** are rare examples of metal promoted C–F activation from PPh₃–*n*(C₆F₅)_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 ¹⁹F NMR (Pt–F, –200 < δ < –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 reaction⁶ is the formation of the oxocarboplatinum [PtMe(2-OC₆F₄PPh₂)(PPh₂(C₆F₅))] from moist [PtMe(THF)(PPh₂–(C₆F₅)₂)]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

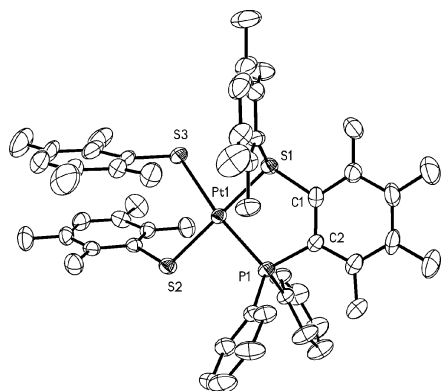


Fig. 2 Structure of [Pt(SC₆HF₄-4)₂(1,2-C₆F₄(SC₆HF₄-4)(PPh₂))] **5**. H atoms are omitted for clarity. Principal bond dimensions (Å and °): Pt1–P1 2.261(2), Pt1–S1 2.268(2), Pt1–S2 2.300(2), Pt1–S3 2.378(2), S1–Pt1–P1 89.91(8), S2–Pt1–S3 97.65(8).

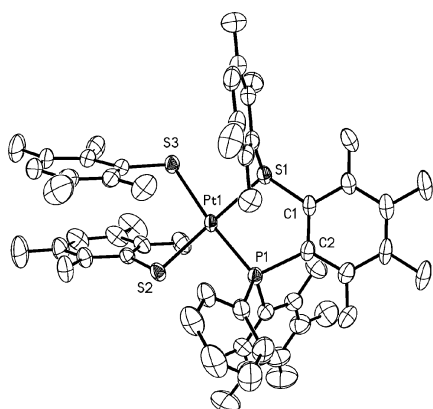


Fig. 3 Structure of [Pt(SC₆HF₄-4)₂(1,2-C₆F₄(SC₆HF₄-4)(PPh(C₆F₅))] **10**. H atoms are omitted for clarity. Principal bond dimensions (Å and °): Pt1–P1 2.2313(14), Pt1–S1 2.2812(14), Pt1–S2 2.3064(15), Pt1–S3 2.3537(14), S1–Pt1–P1 89.41(5), S2–Pt1–P3 96.74(5).

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 C₆F₅ ring is bound to carbon or phosphorus atoms.³

Notes and references

‡ Crystal data. Bruker P4 diffractometer, Mo–K_α (λ = 0.71073 Å), operated at room temp. **8**: C₆₀H₁₄F₃₆P₂Pt₂S₄, MW = 1999.07, hexagonal, P6₃/m, *a* = *b* = 25.675(2), *c* = 19.115(2), *Z* = 6, *D*_{calcd} = 1.825 g cm^{–3}, *R*₁ = 0.0542 for 3631 *I* > 2σ(*I*) and *wR* = 0.1528 for 6577 data, 502 parameters and 28 restraints. **5**: C₃₆H₁₃F₁₆P₂PtS₃, MW = 1071.70, triclinic, P1, *a* = 11.945(3), *b* = 12.0754(14), *c* = 13.4898(18), α = 102.108(10), β = 102.397(17), γ = 105.499(14), *Z* = 2, *D*_{calcd} = 2.027 g cm^{–3}, *R*₁ = 0.0431 for 4627 *I* > 2σ(*I*) and *wR* = 0.1023 for 6109 data and 514 parameters. **10**: C₃₆H₈F₂₁P₂PtS₃, MW = 1161.66, triclinic, P1, *a* = 11.8338(10), *b* = 12.4575(14), *c* = 14.5848(13), α = 96.898(8), β = 107.898(7), γ = 105.595(7), *Z* = 2, *D*_{calcd} = 2.007 g cm^{–3}, *R*₁ = 0.0348 for 5688 *I* > 2σ(*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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