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[2,2'-Bipyridyl]platinum(II) Complexes with Fluorinated Benzenethiolate Ligands: Synthesis and Structural Elucidation

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[2,2′-Bipyridyl]platinum(II) Complexes with Fluorinated Benzenethiolate Ligands: Synthesis and Structural Elucidation

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A series of platinum thiolate complexes of the type [Pt(*bpy*)(SR$_F$)$_2$] (bpy = 2,2′-bipyridyl and SR$_F$ = $^-$SC$_6$F$_5$ (1), $^-$SC$_6$F$_4$-4-H (2)) have been synthesized in good yields by metathetical reactions of [Pt(*bpy*)Cl$_2$] with [Pb(SR$_F$)$_2$], (SR$_F$ = $^-$SC$_6$F$_5$, $^-$SC$_6$F$_4$-4-H) and their crystal structures determined. The effect of the different thiolates in the structural properties of the complexes both in the solid state and in solution have been analyzed. The analyses in solid state suggests that the difference in π–π interactions among the aromatic rings may cause the different arrangements of the molecules in the crystal structures.

Keywords: 2,2′-Bipyridyl (*bpy*); Fluorinated thiolate complexes; Platinum complexes; Crystal engineering; π–π Stacking

INTRODUCTION

2,2′-Bipyridyl (*bpy*) is probably one of the most widely employed ligands in different areas of chemistry including coordination and organometallics [1]. In general this compound coordinates in a N—N chelate fashion, a fact that has attracted the attention of catalytic chemists due to the potential stability that this ligand may confer to the transition metal complexes that are formed [2]. Moreover, *bpy* can be easily functionalized, thus providing a tunable framework both in sterics and electronics [1,3]. The virtues that this ligand and their analogs have shown in these areas have become fundamental on its employment in the relatively new areas of chemistry such as supramolecular chemistry, self assembly and molecular recognition [1,4,5]. This is due to the fact that *bpy* may act as a blocking ligand thus reducing the degrees of freedom and enabling chemists to attain predictable structures that, in combination with transition metals of group 10 (in particular Pd and Pt), may afford highly ordered structures in the solid state [1,3,6,7].

Also the interest and significance that fluorocompounds and the study of their interactions in the life sciences and solid state materials has increased steadily in the last decade, turning out to be a useful tool in crystal engineering [8–12].

In addition, platinum group metal complexes containing *bpy* and monodentated thiolate ligands on its structure are rare [13–17], due in part to the well known tendency of these complexes to polymerize [18], affording in most of the cases intractable solids. Moreover, the chemistry of aromatic sterically hindered thiols has been extensively studied in recent years due to the importance that some of its complexes may play as models for active sites in metalloproteins [19–21]. This is particularly true in the case of nitrogenase, thought to be the key catalyst in the reduction of dinitrogen to ammonia [22–26]. Some complexes have also been used as highly active catalysts in allylic alkylation and C—C coupling reactions [27–29]. Among the sterically hindered thiolate ligands, fluorinated benzenethiols have occupied an important place over other sterically hindered thiols due to the facility with which steric and electronic properties can be tuned by merely changing the fluorine substitution in the aromatic ring [27–33] thus allowing them to stabilize complexes with unusual geometries, oxidation states and intra- or intermolecular interactions [34–37]. Hence, given our continuous interest in the design and synthesis of transition metal complexes including fluorinated thiolates for the fine tuning

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of the electronics and due to the success that we have attained before by using fluorinated anilines [38], we would like to report here the synthesis of complexes of the type [Pt(*bpy*)$(SR_F)_2$] and the potential identification of the electronic effects of the different fluorinated thiolates over the structures of these species in the solid state.

RESULTS

The reaction of one equivalent of the lead salt of the corresponding thiolate [Pb$(SR_F)_2$] ($SR_F = {}^{-}SC_6F_5$, ${}^{-}SC_6F_4$-4-H) with one equivalent of [Pt(*bpy*)$(Cl)_2$] afford complexes [Pt(*bpy*)$(SC_6F_5)_2$] (**1**) [15,39] and [Pt(*bpy*)$(SC_6F_4\text{-}4\text{-}H)_2$] (**2**) in good yields. Both compounds were obtained as analytically pure products from recrystallization of CH_2Cl_2/MeOH solvent systems. Given the similarity in the structures of these complexes, common features in their spectroscopic properties exist. The information obtained from ^{1}H NMR of the series of complexes is not very informative since only common signals due to the presence of the aromatics of the *bpy* ligand are observed between δ 9.98 ppm and 7.63 ppm. Additionally, for complex **2**, a multiplet due to the presence of the proton of the ligands SC_6F_4-4-***H*** is observed between δ 6.77 ppm and 6.65 ppm.

The $^{19}F\{^1H\}$ NMR experiments of the synthesized complexes reveal the fluorinated thiolates to be present, with typical splitting patterns for the ligands ${}^{-}SC_6F_5$ (**1**) and ${}^{-}SC_6F_4$-4-H (**2**) [27]. The observed patterns are in agreement with the proposed formulations. Additionally, analysis by FAB$^+$-Mass spectrometry shows in both cases the molecular ions with the appropriate isotope distribution [40]. Other important peaks in the spectra correspond to the consecutive loss of the two thiolate ligands in both cases at 550 and 532 m/z respectively for (**1**) and (**2**) and at 350 m/z for both complexes. Elemental analyses for both complexes are consistent with the proposed formulations.

Crystals suitable for single crystal X-ray diffraction analysis (Table I) were obtained for both complexes, once again these compounds share a number of molecularly common structural features, but also important differences in their crystal structures. The crystal structure of **1** presents two molecules, from now on referred as Pt1 and Pt2, in the asymmetric unit. In Pt2 one of the SR_F rings is disordered over two positions. Not considering this disordered ring there are no significant differences in geometry between the two molecules (Table II). In **2** only one molecule is present in the asymmetric unit. The molecular structures of **1** and **2** can be defined as slightly distorted square planar, having the platinum centers with the *bpy* ligand coordinated in a bidentate manner and completing the coordination sphere the two thiolates adopting a *cis* conformation, each *trans* to one nitrogen of the *bpy* ligand (Figs. 1 and 2). All bond distances and angles are within the expected values (Table II).

The aromatic rings of the thiolates are not coplanar, the angle between the planes of the rings is 9.28° and 7.08° for (**1**) and (**2**), respectively. The planes of the rings lie approximately normal to the plane of the *bpy* rings (dihedral angles 80.70° and 86.84° (**1**) and 81.16° and 87.23° (**2**)). The closest intermolecular Pt···Pt distances are 5.692 Å and 4.508 Å for **1** and **2.**

The crystal packing of both molecules **1** and **2** is very different, this difference can be explained

TABLE I Summary of crystal structure data for complexes [Pt(*bpy*)$(SC_6F_5)_2$] (**1**) and [Pt(*bpy*)$(SC_6F_4\text{-}4\text{-}H)_2$] (**2**)

Empirical formula	$C_{44}H_{16}F_{20}N_4Pt_2S_4$ (**1**)	$C_{22}H_{10}F_8N_2PtS_2$ (**2**)
Formula weight	1499.03	713.53
Temperature, K	291(2)	291(2)
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	C2/c
a, Å	13.2912(6)	26.5091(14)
b, Å	17.4189(8)	12.8298(7)
c, Å	19.2070(9)	14.3716(7) Å
β o	98.744(1)	118.373(1)
Volume, Å^3	43.95.1(4)	4300.7(4)
Z	4	8
Density (calc.), g/cm^3	2.265	2.204
μ, mm^{-1}	6.676	6.803
F(000)	2832	2704
Reflections collected	35641	17324
Independent reflections	7733 [R(int) = 0.1235]	3792 [R(int) = 0.0428]
Max. and Min. Trans.	0.7549 and 0.3601	0.2781 and 0.1402
Absorption correction	Analytical	Integration
Data/restraints/parameters	7733 / 0 / 661	3792 / 0 / 316
Goodness-of-fit on F^2	0.683	0.954
Final R indices [I > 2σ (I)]	R1 = 0.0406, wR2 = 0.0602	R1 = 0.0274, wR2 = 0.0434
R indices (all data)	R1 = 0.0842, wR2 = 0.0677	R1 = 0.0371, wR2 = 0.0450
Largest diff. peak/hole, eÅ^{-3}	1.294/−0.640	0.776/−0.777

TABLE II Selected bond lengths (Å) and angles (°) for [Pt(*bpy*)(SC_6F_5)$_2$] (**1**) and [Pt(*bpy*)(SC_6F_4-4-H)$_2$] (**2**)

1 (Molecule Pt1)		**1** (molecule Pt2)		**2**	
Pt(1)-N(1)	2.052(7)	Pt(2)-N(25)	2.050(7)	Pt(1)-N(1)	2.064(4)
Pt(1)-N(7)	2.047(6)	Pt(2)-N(31)	2.046(7)	Pt(1)-N(7)	2.066(3)
Pt(1)-S(1)	2.270(3)	Pt(2)-S(3)	2.294(2)	Pt(1)-S(1)	2.282(1)
Pt(1)-S(2)	2.300(2)	Pt(2)-S(4)	2.315(5)	Pt(1)-S(2)	2.295(1)
		Pt(2)-S(4A)	2.269(6)		
N(7)-Pt(1)-N(1)	79.7(3)	N(31)-Pt(2)-N(25)	78.5(3)	N(7)-Pt(1)-N(1)	78.9(1)
S(1)-Pt(1)-S(2)	94.64(9)	S(3)-Pt(2)-S(4)	95.90(13)	S(1)-Pt(1)-S(2)	89.81(5)
		S(4A)-Pt(2)-S(3)	93.00(15)		
N(1)-Pt(1)-S(1)	91.5(2)	N(31)-Pt(2)-S(3)	95.2(2)	N(1)-Pt(1)-S(1)	94.8(1)
N(7)-Pt(1)-S(2)	94.3(2)	N(25)-Pt(2)-S(4)	89.8(2)	N(7)-Pt(1)-S(2)	96.1(1)
		N(25)-Pt(2)-S(4A)	94.1(2)		
N(1)-Pt(1)-S(2)	173.9(2)	N(25)-Pt(2)-S(3)	172.3(2)	N(1)-Pt(1)-S(2)	174.2(1)
N(7)-Pt(1)-S(1)	169.0(2)	N(31)-Pt(2)-S(4)	166.0(2)	N(7)-Pt(1)-S(1)	171.9(1)
		N(31)-Pt(2)-S(4A)	165.5(2)		

by considering the organization of the aromatic rings in the crystal structures as shown in Figs. 3 and 4. In **1** the aromatic rings SR_F of both molecules Pt1 and Pt2 do not present intramolecular interaction between them; as indicated by the long centroid···centroid distances, Cg···Cg, of 4.25 Å and 4.14 Å, respectively.

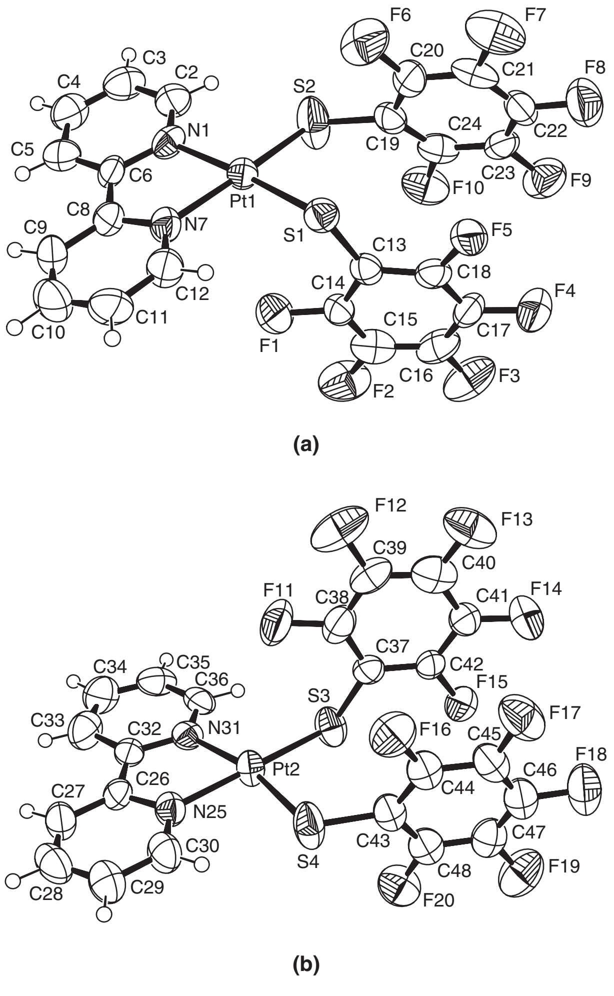


FIGURE 1 An ORTEP representation, showing the atom labeling scheme, of the structure of the two independent molecules in [Pt(*bpy*)(SC_6F_5)$_2$] (**1**) at 50% probability, H atoms are shown as circles of arbitrary radius. In (b) for clarity only the major component of the disordered ring ($S4R_F$) is shown.

One of the aromatic rings of Pt2, $S3R_F$, is below the ring $S10R_F$ of a Pt1 molecule at $(-1/2 + x, 3/2 - y, 1/2 + z)$, and the ring $S4R_F$ is on top of the N1-pyridine ring of a Pt1-*bpy* molecule at $(x, 1 + y, z)$. On the other side both *bpy* rings of Pt2 are on top the *bpy* rings of another Pt2 molecule at $(1 - x, 2 - y, 1 - z)$.

In **2** the relations are more simple, the SR_F groups present an intramolecular π–π interaction between them (Table III). Their crystal packing shows the SR_F rings of one molecule on top of the SR_F ring of another molecule at $(-x, 1 - y, 1 - z)$. The aromatic rings of the *bpy's* are on top of the *bpy* rings of another molecule at $(-x, y, 1/2 - z)$.

DISCUSSION

C. Janiak [41] reported a geometrical analysis on π–π stacking in metal complexes with aromatic nitrogen-containing ligands based on a Cambridge Structural Database search. He found that a face-to-face π–π alignment where most of the ring-plane area overlaps is a rare phenomenon and that the usual π interaction is an offset or slipped stacking, i.e., the rings are parallel

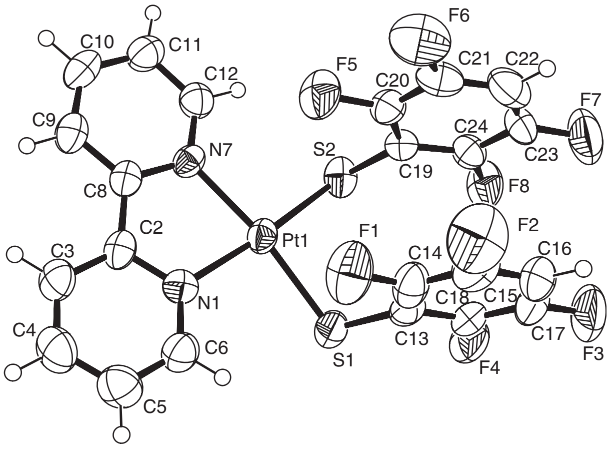


FIGURE 2 An ORTEP representation, showing the atom labeling scheme, of the structure of [Pt(*bpy*)(SC_6F_4-4-H)$_2$] (**2**) at 50% probability, H atoms are shown as circles of arbitrary radius.

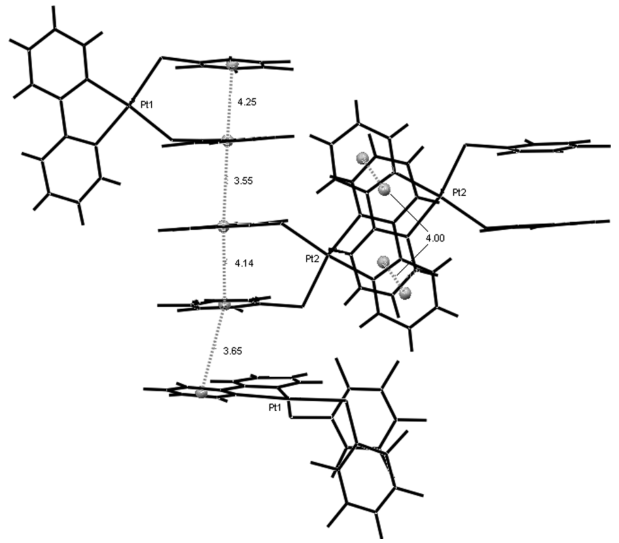


FIGURE 3 Representation of the aromatic rings organization, with centroid–centroid distances (Å), for complex **1**.

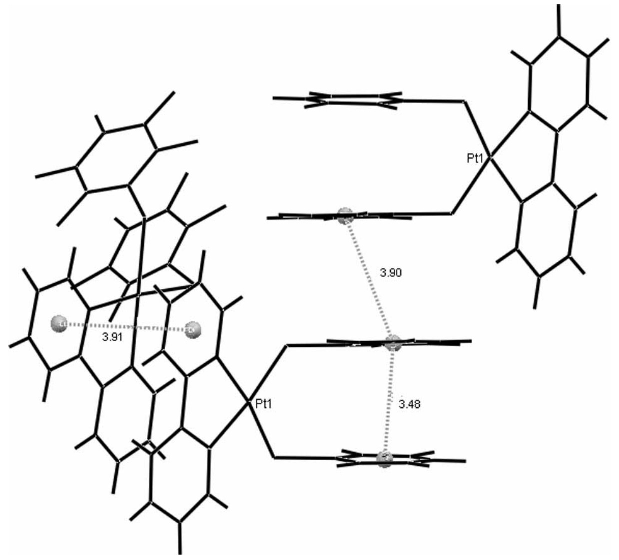


FIGURE 4 Representation of the aromatic ring organization, including centroid–centroid distances (Å), for complex **2**.

displaced. The ring normal and the vector between the ring centroids form an angle of about 20° up to centroid–centroid distances of 3.8 Å. The following discussion is based on these values and the consideration that similar distances and angles will indicate π–π interactions for the SR_F aromatic rings.

From a molecular point of view the main difference between **1** and **2** is that in **2** the SR_F rings have a geometry that is in agreement with an intermolecular π–π interaction between them (Table III). This suggests that the presence of a H atom in the SR_F rings of **2** allows the molecules to find a geometry where an attractive interaction between them is possible, while this is not possible in **1**. It is noteworthy that the fluorinated thiolate rings of the related Pt(II)-dppf (dppf = diphenylphosphineferrocene) complex with perfluorinated thiophenols, $[Pt(dppf)(SC_6F_5)_2]$ [35] also does not show π stacking in the solid state.

The presence of two different molecules in **1** is related to the different interactions they show in the crystal structure. The SR_F rings exhibit π–π interactions with two different aromatic rings of two other molecules. One of them interacts with an SR_F ring of another molecule, but now the S atoms point in the opposite directions allowing a positive dipole of one molecule to interact with the negative dipole of the other. The other SR_F rings interact with the pyridine ring of another molecule once more in a geometry that allows the interaction of opposite dipoles (Fig. 5). It is interesting that these important differences are due to the mere presence of an extra fluorine atom in the aromatic ring.

The other possible interactions between the aromatic rings in **1** and **2** can hardly be considered as π–π interactions and their presence may be due more to a geometric close packing of the molecules (van der Waals interactions), than significant π–π interactions.

Additionally, Janiak and co-workers have recently reported on the importance of C—H···F—C hydrogen bonds [12] and although this kind of interaction does not seem to be relevant in this study (Table IV) their potential relevance can not be ruled out and

TABLE III Geometry of π–π interactions

1 Cg(I)–Cg(J)	Cg–Cg (Å)[†]	α(°)[‡]	β(°)[¶]	γ(°)[§]	(Å)[‖]	(Å)[#]
Cg(C37–C42)–Cg(C13–C18)[††]	3.552(6)	0.58	17.89	17.32	3.390	3.380
Cg(C43–48)–Cg(N1/C2–C6)[‡‡]	3.648(9)	6.67	24.74	21.16	3.402	3.313
Cg(C13–C18)–Cg(C19–C24)	4.253(6)	9.34	46.77	37.95	3.354	2.914
Cg(C37–C42)–Cg(C43–C48)	4.143(10)	7.24	43.05	35.82	3.361	3.028
Cg(N25/C26–C30)–Cg(N31/C32–C36)[¶¶]	4.004(6)	4.26	28.44	32.70	3.370	3.521
2						
Cg(C13–C18)–Cg(19–24)	3.478(3)	7.08	12.43	19.51	3.278	3.397
Cg(N1/C2–C6)–Cg(N7/C8–C12)[§§]	3.905(3)	3.68	27.90	29.02	3.415	3.451
Cg(C19)–Cg(C19–C24)[‖‖]	3.899(3)	19.84	19.84	3.667	3.667	1.323

[†] Dihedral angle between planes I and J. [‡] Angle between Cg(I)–Cg(J) vector and normal to plane I. [¶] Angle between Cg(I)–Cg(J) vector and normal to plane J. [§] Distance between ring centroids. [‖] Perpendicular distance of Cg(I) on ring J. [#] Perpendicular distance of Cg(J) on ring I. [††] − 1/2 + x, 3/2 − y, 1/2 + z. [‡‡] x, 1 + y, z. [¶¶] 1 − x,2 − y,1 − z. [§§] − x,y,1/2 − z. [‖‖] − x,1 − y,1 − z.

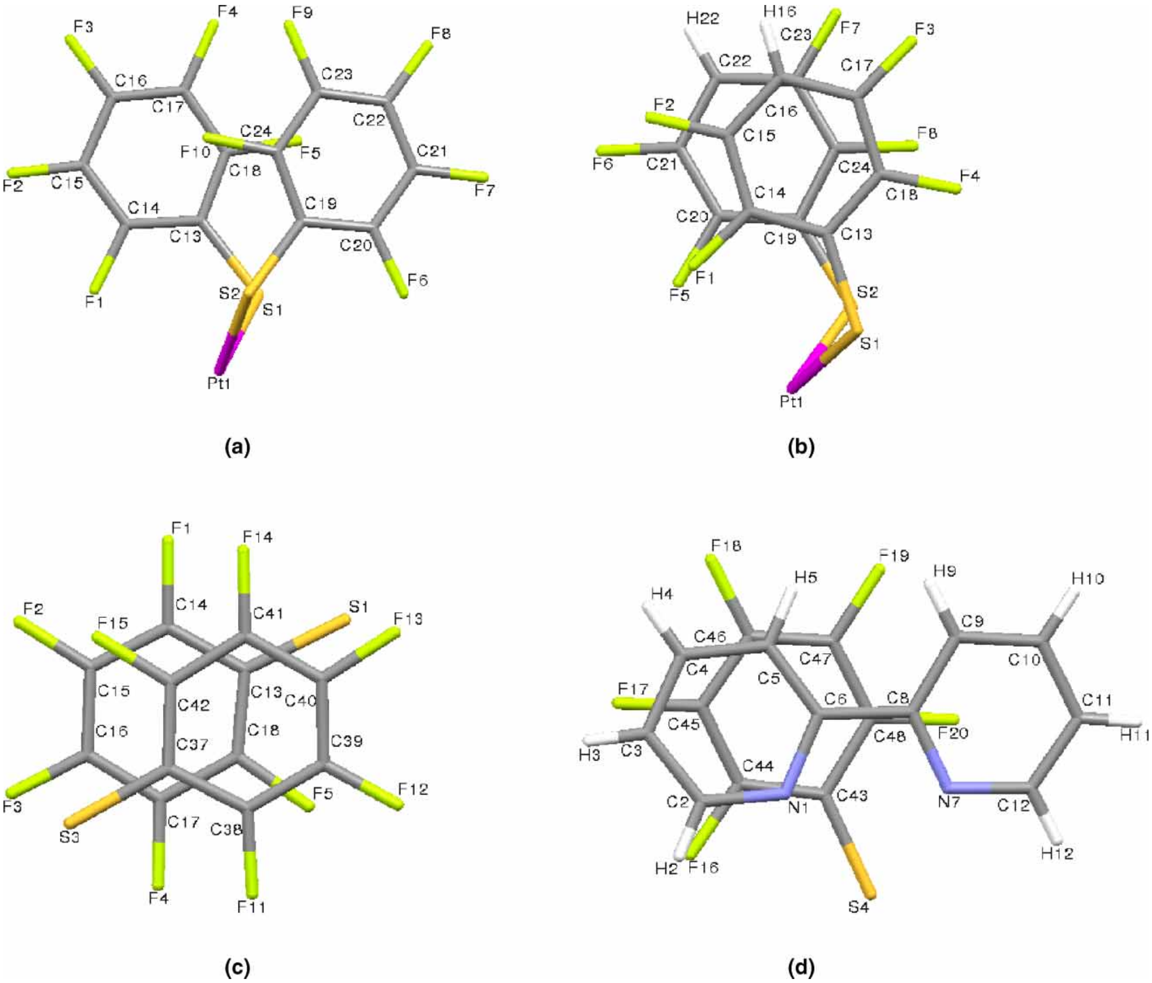


FIGURE 5 Representation of: (a) repulsive intramolecular interaction between SR_F rings in **1**; (b) intramolecular π−π interactions between the SR_F rings in **2**; (c) intermolecular π−π interactions in between $S1R_F$ and $S3R_F$ rings in **1**; (d) intermolecular π−π interactions in between SR_F-py rings **1**.

further studies similar to those reported by Janiak have to be performed in order to weigh the real repercussions of these bonds on the solid state structures.

In summary, we have reported an efficient and facile, high yield synthetic procedure for the synthesis of monomeric [Pt(*bpy*)(SR_F)$_2$] complexes and studied the effect of having fluorinated thiophenolates on their structures in the solid state. The simple presence of one extra F atom in one of the molecules has an important influence in molecular packing that can be explained through π−π interactions of the aromatic rings. Due to the importance that palladium compounds have had in metal mediated organic synthesis efforts aimed to employ these compounds in C—C, C—S and C—N cross coupling reactions are currently under investigation.

TABLE IV Hydrogen bonds (Å, °) for: **1** and **2.**

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/°	Symmetry operation for A
1					
C4-H4…F4	0.9300	2.4400	3.132(12)	131.00	−1 + x,y,z
C5-H5…F11	0.9300	2.5500	3.472(12)	173.00	−1/2 + x,3/2 − y, − 1/2 + z
C9-H9…F11	0.9300	2.3400	3.271(12)	177.00	−1/2 + x,3/2 − y, − 1/2 + z
C36-H36… F4	0.9300	2.5300	3.127(11)	123.00	−1/2 + x,3/2 − y,1/2 + z
2					
C3-H3…F5	0.9300	2.3500	3.138(7)	143.00	−x, − y,1 − z
C9-H9…F5	0.9300	2.4000	3.240(6)	149.00	−x, − y,1 − z

EXPERIMENTAL

Materials and Methods

Unless stated otherwise, all reactions were carried out in the open air, solvents were dried using established procedures [42] and distilled under dinitrogen immediately prior to use. The IR spectra were recorded on a Nicolet-Magna 750 FT-IR spectrometer as nujol mulls. The ^{1}H NMR (300 MHz) spectra were recorded on a JEOL GX300 spectrometer. Chemical shifts are reported in ppm down field of TMS using the solvent ($CDCl_3$, $\delta = 7.27$) as an internal standard. $^{19}F\{^1H\}$ NMR spectra were recorded with complete proton decoupling and are reported in ppm using C_6F_6 as an external standard. Elemental analyses were determined on a Perkin–Elmer 240. Positive-ion FAB mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operated at an accelerating voltage of 10 Kv. Samples were desorbed from a nitrobenzyl alcohol (NOBA) matrix using 3 KeV xenon atoms. Mass measurements in FAB are performed at a resolution of 3000 using magnetic field scans and the matrix ions as the reference material or, alternatively, by electric field scans with the sample peak bracketed by two (polyethylene glycol or cesium iodide) reference ions.

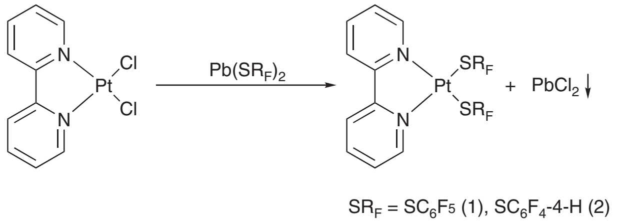
The 2,2′-bipyridyl (*bpy*), HSC_6F_5, HSC_6F_4-4-H and K_2PtCl_4 were obtained commercially from Aldrich Chem. Co and Pressure Chemical Co. respectively. Compounds [Pt(*bpy*)Cl_2] [43] and [Pb($SR_F)_2$] [44] R_F = C_6F_5, C_6F_4-4-H were synthesized according to the published procedures.

General Procedure for the Synthesis of the Complexes [Pt(bpy)($SR_F)_2$]

All the complexes were obtained using the same experimental procedure. As a representative example the synthesis of [Pt(*bpy*)($SC_6F_5)_2$] is described (Scheme 1).

Synthesis of [Pt(bpy)($SC_6F_5)_2$] (1)

To a solution of [Pt(*bpy*)(Cl)$_2$] (50.0 mg, 0.1184 mmol) in acetone (20 mL), a solution of [Pb($SC_6F_5)_2$] (72 mg, 0.1184 mmol) in acetone (20 mL) was added dropwise under stirring, the resulting red-brick solution was allowed to stir overnight, after which time the solution was filtered through a short plug of Celite® and the solvent removed under vacuum. The residue was recrystallized from CH_2Cl_2-hexane, to afford **1** as a deep red microcrystalline powder. Yield 64.5%. M.p. = 251–254°C; NMR-^{1}H (300 MHz, $CDCl_3$), δ 9.98–9.84 (*m*, *bpy*, 2H), 8.22–8.16 (*m*, *bpy*, 4H), 7.68–7.63 (*m*, *bpy*, 2H); NMR-$^{19}F\{^1H\}$ (282 MHz, $CDCl_3$), δ −131.87 (*m*, $^3J_{Fo\text{-}Fm} = 19.74$ Hz, *o*-F), −160.12 (*t*, $^3J_{Fm\text{-}Fp} = 19.74$ Hz, *p*-F), −166.87 (*m*, $^4J_{Fo\text{-}Fp} = 5.64$, *m*-F). Elem. Anal. Calculated for [$C_{22}H_8F_{10}N_2Pt_1S_2$] Calc.%: C: 35.25, H: 1.08. Found%: C: 34.92.14, H: 1.06. MS-FAB$^+$ [M$^+$] = 749 (25%) *m/z*.



SCHEME 1 Metathesis Reactions for the synthesis of the complexes [Pt(*bpy*)($SR_F)_2$].

Synthesis of [Pt(bpy)(SC_6F_4-4-H$)_2$] (2)

[Pt(*bpy*)(Cl)$_2$] (50.0 mg, 0.1184 mmol) in acetone (20 mL), a solution of [Pb(SC_6F_4-4-H$)_2$] (67.4 mg, 0.1184 mmol) in acetone (20 mL). M.p. = 255–256°C. Yield 60.7%. NMR-^{1}H (300 MHz, $CDCl_3$), δ 10.00–9.87 (*m*, *bpy*, 2H), 8.21–8.19 (*m*, *bpy*, 4H), 7.70–7.65 (*m*, *bpy*, 2H), 6.77–6.65 (*m*, *SC$_6$F$_4$-4-**H***, 2H); NMR-$^{19}F\{^1H\}$ (282 MHz, $CDCl_3$), δ −132.48 (*m*, *o*-F), −140.85 (*m*, *m*-F). Elem. Anal. Calculated for [$C_{22}H_{10}F_8N_2Pt_1S_2$] Calc.%: C: 37.03, H: 1.41. Found%: C: 37.06, H: 1.42. MS-FAB$^+$ [M$^+$] = 713 (5%) *m/z*.

Data Collection and Refinement for [Pt(bpy)($SC_6F_5)_2$] (1) and [Pt(bpy)(SC_6F_4-4-H$)_2$] (2)

Crystalline red–orange prisms of **1** and **2** were grown independently by slow evaporation of CH_2Cl_2/MeOH solvent systems, and mounted on glass fibers. In all cases, the X-ray intensity data were measured at room temperature on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å). The detector was placed at a distance of 4.837 cm from the crystals in all cases. A total of 1800 frames were collected with a scan width of 0.3° in ω and an exposure time of 10 sec/frame. The frames were integrated with the Bruker SAINT software package [45] using a narrow-frame integration algorithm. The integration of the data was done using a monoclinic unit cell in both cases to yield a total of 35641 and 17324 reflections for **1** and **2** respectively to a maximum 2θ angle of 50.00° (0.93 Å resolution), of which 7733 (**1**) and 3792 (**2**) were independent. Analysis of the data showed in all cases negligible decays during data collections. The structures were solved by direct methods using the SHELXS-97 [46] program. The remaining atoms were located via a few cycles of least squares refinements and difference Fourier maps, using the space group *P2$_1$/n* with $Z = 4$ for **1** and *C2/c* with $Z = 8$ for **2**. The S4R$_F$ in **1** was refined with statistical disorder over two positions with site occupancies of 0.60 (S4,C43–C48, F16–F20) and 0.40 (S4A,C43A–C48A, F16A–F20A). Hydrogen atoms were input at calculated positions, and allowed to ride on the atoms to which they are attached. Thermal parameters were refined for hydrogen atoms on the phenyl groups using a Ueq = 1.2 Å to the preceding atom in all cases. For all complexes, the final cycle of refinement was carried out on all non-zero data using SHELXL-97 [46] and anisotropic thermal parameters for all non-hydrogen atoms. The details of the structure determinations are given in Table I and selected bond lengths (Å) and angles (°) are given in Table II. The numbering of the atoms is shown in Figs. 1 and 2 respectively (ORTEP) [47]. CCDC 638434 and 638435 contain the supplementary crystallographic data for **1** and **2**. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk

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