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Palladium(II) Compounds with Fluorinated Pincer-Type (SCS) Ligands: X-ray Structures of C_6H_4-1,3-$(CH_2SC_6H_4F$-4$)_2$ and [PdCl(SCS–R_f)] [R_f = C_6H_4F-2, C_6H_4F-3, C_6H_4F-4, $C_6H_4(CF_3)$-2, and $C_6H_4(CF_3)$-4]

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Metathesis reactions employing lead fluorothiolates and C_6H_4-1,3-$(CH_2Br)_2$ afford the corresponding pincer-type dithioether ligands C_6H_4-1,3-$(CH_2SR_f)_2$ [R_f = C_6H_4F-2 (**L1**), C_6H_4F-3 (**L2**), C_6H_4F-4 (**L3**), $C_6H_4CF_3$-2 (**L4**), $C_6H_4CF_3$-3 (**L5**), and $C_6H_4CF_3$-4 (**L6**)]. A series of Pd^{II} pincer-type complexes [PdCl(κ^3-**Ln**)], **1** to **6**, were prepared and fully characterized. The X-ray diffraction molecular structures of C_6H_4-1,3-$[CH_2S(C_6H_4F$-4$)]_2$ (**L3**), [PdCl(SCS–C_6H_4F-2)] (**1**), [PdCl(SCS–C_6H_4F-3)] (**2**), [PdCl(SCS–C_6H_4F-4)] (**3**), [PdCl{SCS–$C_6H_4(CF_3)$-2}] (**4**), and [PdCl{SCS–$C_6H_4(CF_3)$-4}] (**6**) are also reported.

Introduction

Pincer-type palladacycles are one of the most popular and well-investigated classes of cyclometalated compounds.[1,2] They have found application in diverse areas from efficient catalyst precursors[3] to molecular materials for crystalline switches and sensors.[4] In particular, SCS pincer-type palladium compounds have been widely studied as catalyst precursors, either as low-molecular-weight or PEG-supported polymers,[2a,5] for Pd^{II}-catalyzed Heck[6] and Suzuki[2d,7] cross-coupling reactions.[8–10] SCS pincer-type palladium compounds have also been the focus of interesting structural and conformational studies such as isomeric exchange[11] and dimer formation.[12] Macromolecular and self-assembled supramolecular chemistry have also profited from the useful properties of SCS pincer-type compounds for the construction of polymetallic complexes,[13] macrocycles,[14] large metallodendrimers,[15] functionalized polymers,[16] mixed Pd–Au nanoparticles,[17] polypincer-porphyrin compounds,[18] and supramolecular arrays of palladium.[19]

The possibility of fine tuning the steric and electronic properties of the metal center by simply changing the donor groups or their substituents is one of the features that makes this anionic, terdentate, six-electron donor ligand so flexible and amenable to a plethora of applications.[20] In particular, fluorine-containing pincer-type complexes are relatively rare.[21] The fluorous SCS pincer-type palladium complex with a SCS–C_6H_4-*p*-C_6F_{13} ligand has recently been synthesized and shown to be catalytically active under both microwave and thermal heating.[22] The fluorinated PCP pincer-type complexes [RuCl{C_6H_3-2,6-[$CH_2P(C_6F_5)_2]_2$}-(PPh_3)],[23a] [PdCl{C_6H_3-2,6-[$CH_2P(C_6F_5)_2]_2$}], and [Pd-($NCCH_3$){C_6H_3-2,6-[$CH_2P(C_6F_5)_2]_2$}]BF_4 have also recently been described.[23b]

As part of our interest in fluorinated sulfur-containing ligands,[24] we have synthesized a series of SCS pincer-type ligands with several fluorinated substituents at the sulfur atoms.[25] In this paper, we report on the synthesis and characterization of the pincer-type dithioether ligands C_6H_4-1,3-$(CH_2SR_f)_2$ [R_f = C_6H_4F-2 (**L1**), C_6H_4F-3 (**L2**), C_6H_4F-4 (**L3**), $C_6H_4(CF_3)$-2 (**L4**) $C_6H_4(CF_3)$-3 (**L5**), and $C_6H_4(CF_3)$-4 (**L6**)] and the corresponding Pd^{II} complexes [PdCl(**Ln**)], **1** to **6**, and include the X-ray diffraction structures of C_6H_4-1,3-$(CH_2SC_6H_4F$-4$)_2$ (**L3**), [PdCl(SCS–C_6H_4F-2)] (**1**), [PdCl(SCS–C_6H_4F-3)] (**2**), [PdCl(SCS–C_6H_4F-4)] (**3**), [PdCl{SCS–$C_6H_4(CF_3)$-2}] (**4**), and [PdCl{SCS–$C_6H_4(CF_3)$-4}] (**6**).

Results and Discussion

SCS Pincer-Type Ligands

Lead fluorothiolates, $Pb(SR_f)_2$, react with C_6H_4-1,3-$(CH_2Br)_2$ to give the corresponding dithioether compounds C_6H_4-1,3-$(CH_2SR_f)_2$ [R_f = C_6H_4F-2 (**L1**), C_6H_4F-3 (**L2**), C_6H_4F-4 (**L3**), $C_6H_4(CF_3)$-2 (**L4**), $C_6H_4(CF_3)$-3 (**L5**), and $C_6H_4(CF_3)$-4 (**L6**)] as clear dense oils (**L1**, **L2**, **L4**, and **L5**)

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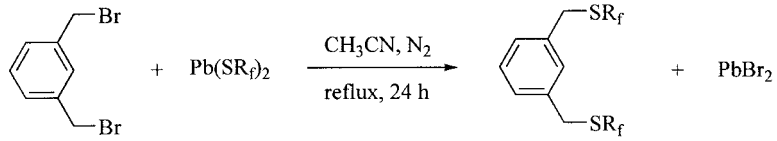


L1 $R_f = C_6H_4F$-2
L2 $R_f = C_6H_4F$-3
L3 $R_f = C_6H_4F$-4
L4 $R_f = C_6H_4(CF_3)$-2
L5 $R_f = C_6H_4(CF_3)$-3
L6 $R_f = C_6H_4(CF_3)$-4

Scheme 1. Synthesis of dithioether compounds **L1**–**L6**.

or crystalline white solids (**L3** and **L6**), in very good yields (see Scheme 1).

The mass spectra of all compounds show the signals corresponding to the molecular ion $[M]^+$ with significant intensities (75–90%). The ^1H NMR spectra of compounds **L1**–**L6** exhibit a singlet for the benzylic CH_2 protons. All other signals appear in the aromatic region as multiplets. The ^{13}C NMR spectra show quartets for the carbon atoms of the CF_3 groups, whereas the signals for all aromatic carbon atoms with fluorine atoms appear as doublets as a result of their magnetic coupling with the fluorine nuclei. The remaining signals have been assigned with the aid of two-dimensional HETCOR experiments. As expected, the ^{19}F NMR spectra for all compounds show only one signal. IR, ^1H and ^{19}F NMR spectroscopy as well as EI-MS data (reported in the Experimental Section) confirm the identity of each ligand.

The X-ray structure of C_6H_4-1,3-$(CH_2SC_6H_4F$-4$)_2$ (**L3**) is shown in Figure 1 and Figure 2, and the principal bond lengths and angles are reported in Table 1. The solid-state structure analysis of compound **L3** corresponds to the results obtained from ^1H, ^{13}C, and ^{19}F NMR spectroscopy, observed in solution.

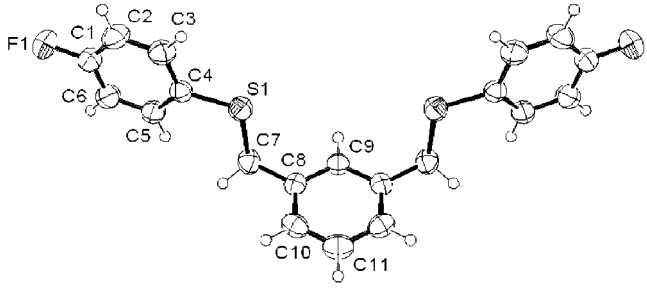


Figure 1. ORTEP drawing of compound C_6H_4-1,3-$(CH_2SC_6H_4F$-4$)_2$ (**L3**).

In contrast with the structure of C_6H_4-1,3-$(CH_2SC_6F_5)_2$,[25] in which the SR_f groups are positioned on opposite sides of, and almost parallel to, the central aromatic ring, the molecular structure of **L3** has a *syn* configuration where the sulfur substituents point in the same direction as and are almost perpendicular to the central aromatic ring.

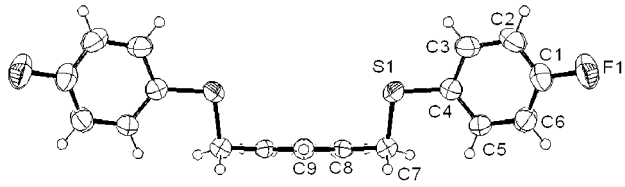


Figure 2. ORTEP drawing of compound **L3**, view along the C9–C11 axis.

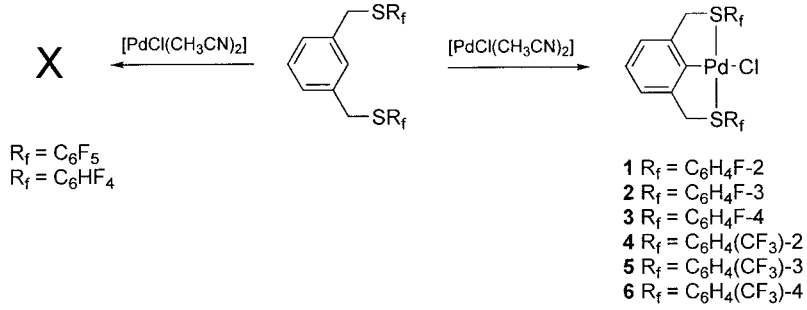
Table 1. Selected bond lengths [Å] and angles [°] for compound C_6H_4-1,3-$(CH_2SC_6H_4F$-4$)_2$ (**L3**).

Bond	Length	Atoms	Angle
S(1)–C(4)	1.770(3)	C(4)–S(1)–C(7)	104.26(12)
S(1)–C(7)	1.809(3)	C(3)–C(4)–S(1)	116.3(2)
C(9)–C(8)	1.389(3)	C(5)–C(4)–S(1)	125.2(2)
C(8)–C(10)	1.383(3)	C(8)–C(7)–S(1)	106.84(17)
C(10)–C(11)	1.376(3)	C(9)–C(8)–C(7)	121.1(2)
C(4)–C(3)	1.389(4)	C(10)–C(8)–C(7)	120.2(2)
C(4)–C(5)	1.379(3)	C(5)–C(4)–C(3)	118.5(3)
C(5)–C(6)	1.380(4)	C(1)–C(6)–C(5)	119.1(3)
C(6)–C(1)	1.355(4)	C(1)–C(2)–C(3)	118.5(3)
C(1)–C(2)	1.366(4)	C(6)–C(1)–C(2)	122.2(3)
C(3)–C(2)	1.372(4)	F(1)–C(1)–C(2)	118.8(3)
F(1)–C(1)	1.355(3)	F(1)–C(1)–C(6)	119.0(3)
		C(10)–C(8)–C(9)	118.8(2)

Pincer-Type Palladacycles

In our experiments, the reaction of the highly fluorinated pincer-type ligands C_6H_4-1,3-$(CH_2SC_6F_5)_2$ or C_6H_4-1,3-$(CH_2SC_6HF_4$-4$)_2$[25] with either $[PdCl_2(NCCH_3)_2]$ or $[Pd(NCCH_3)_4](BF_4)_2$ failed to produce the expected palladacycle derivatives. SC_6F_5 or SC_6HF_4-4 are much poorer donors than the corresponding protioaryl systems and, in contrast to phosphanes, they are not considered to be particularly good π acceptors.[26] Both of these effects contribute to a weaker S–Pd bond than the competing Pd–$NCCH_3$ interactions and prevent the formation of the Pd pincer-type compounds. This lack of reactivity emphasizes the importance of sulfur coordination as a preliminary step to C–Pd bond formation.

In contrast, the reaction of ligands **L1**–**L6** with $[PdCl_2(NCCH_3)_2]$ yielded the corresponding SCS pallada-



Scheme 2. Synthesis of palladium compounds **1**–**6**.

cycle compounds shown below as air-stable, yellow, crystalline solids. The yields are noticeably different for compounds bearing monofluorinated rings (**1**: 96, **2**: 81, **3**: 68%) from those with the bulkier $C_6H_4CF_3$ moiety (**4**: 79, **5**: 36, **6**: 44%), probably because they are influenced by steric factors (Scheme 2).

The ^1H NMR spectra of compounds **1**–**6** in CD_3CN show a broad singlet for the CH_2SR_f protons in the $\delta \approx$ 4.2–4.7 ppm range, probably because of a combination of *syn–anti* isomer exchange and the conformational interconversion of the Pd^{II}-containing five-membered rings.[27] The signal for the proton at ca. 7 ppm (C1–H) is absent, indicating complete cyclopalladation. With the exception of compound **4**, for which the low solubility precluded its measurement, the C1 shielding, as a result of cyclopalladation for the rest of the complexes, is also diagnostic of palladation at C1. The (δ^{13}C1–H – δ^{13}C1–Pd) values are as follows: **1** 28.29; **2** 30.74; **3** 33.57; **5** 30.37; and **6** 30.91 ppm. Likewise, the parameters defined as $\Delta_{Ln} = \delta^{13}C1 - \delta^{13}C4$ for the ligands and $\Delta_n = \delta^{13}C1 - \delta^{13}C4$ for the palladium complexes have the following values: $\Delta_{L1} = 0.74$, $\Delta_1 = 34.08$; $\Delta_{L2} = 0.57$, $\Delta_2 = 35.86$; $\Delta_{L3} = 0.87$, $\Delta_3 = 37.09$; $\Delta_{L5} = 0.63$, $\Delta_5 = 35.3$; and $\Delta_{L6} = 0.44$, $\Delta_6 = 35.87$ ppm.

$^{19}F\{^1H\}$ NMR spectra of compounds **1**–**3** and **4**–**6** exhibit a single, sharp resonance in the fluoro-aromatic region (–108.89, –113.69, –114.6 ppm) or in the CF_3-aromatic region (–56.56, –62.99, –62.60 ppm), respectively. Thus, isomers arising from substituent orientation relative to the square plane are not detected, which suggests that, in these complexes, sulfur inversion is either absent or faster than the NMR time scale. Palladium complexes of related thioethers exhibit relatively low energies for the process involving the inversion of configuration at the sulfur atoms ($\Delta E \approx 50$–70 kJ mol^{-1}), which is probably also true in these cases.[28]

Molecular Structures

An X-ray structural study of compounds **1**–**3** provided solid-state evidence verifying the solution results and confirming, for all cases, the terdentate-binding mode of the SCS ligands. ORTEP drawings of [PdCl(SCS–C_6H_4F-2)] (**1**), [PdCl(SCS–C_6H_4F-3)] (**2**), and [PdCl(SCS–C_6H_4F-4)] (**3**) are shown in Figure 3, Figure 4 and Figure 5, respectively, and selected bond lengths and angles are reported in Table 2.

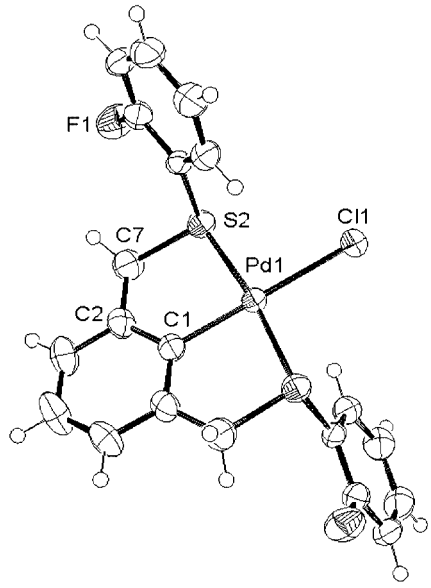


Figure 3. ORTEP drawing of compound [PdCl(SCS–C_6H_4F-2)] (**1**).

The Pd atoms are in slightly distorted square-planar environments: S(1)–Pd(1)–S(2), **1** 171.94(6); **2** 170.84(3); **3** 170.28(2)° and Cl(1)–Pd(1)–C(1), **1** 180.00(1); **2** 177.83(10); **3** 179.03(7)°. The bonding parameters of Pd are very similar to those observed for the complexes [PdCl{2,6-C_6H_3-(CH_2S*t*Bu)$_2$}],[29] Pd–S 2.308(2); Pd(1)–Cl(1) 2.406(3); and Pd–C(1) 1.998(11) Å; [PdCl{2,3,5,6-C_6H-(CH_2S*t*Bu)$_4$}],[19f] Pd–S(1) 2.297(3); Pd(1)–S(2) 2.302(3); Pd(1)–Cl(1) 2.408(3); Pd–C(1) 1.994(9) Å; and [Pd{4-(*n*BuO)-2,6-C_6H_2-(CH_2SPh)$_2$}($NCCH_3$)]$^+$,[30] Pd–S(1) 2.2992(8); Pd–S(2) 2.2961(9); Pd–C(1) 1.975(2) Å.

The C_6H_4F-2 and C_6H_4F-3 groups attached to the metal-bound sulfur atoms in **1** and **2** are oriented in an *anti* fashion with respect to the square plane; a common conformation observed in these type of compounds,[19f,29–31] which allows for minimization of any steric repulsions between the aromatic rings. In contrast, the C_6H_4F-4 groups attached to the metal-bound sulfur atoms in **3** are oriented in a *syn* fashion with respect to the square plane; this allows for maximization of intermolecular aromatic π-stacking inter-

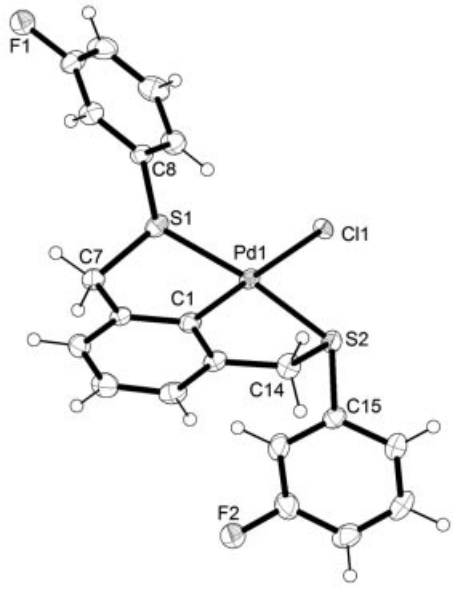


Figure 4. ORTEP drawing of compound [PdCl(SCS–C_6H_4F-3)] (**2**).

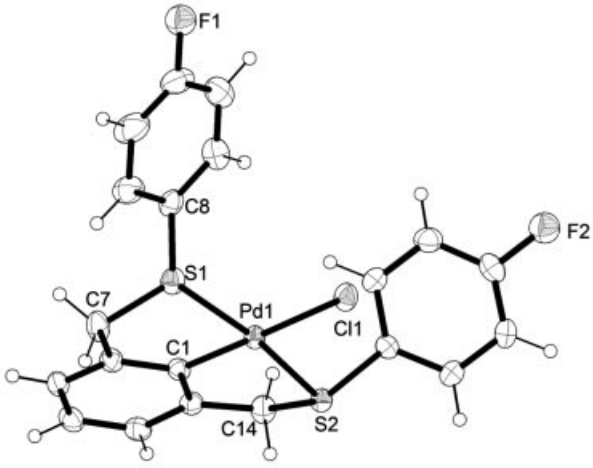


Figure 5. ORTEP drawing of compound [PdCl(SCS–C_6H_4F-4)] (**3**).

Table 2. Selected bond lengths [Å] and angles [°] with estimated standard deviations for complexes **1**, **2**, and **3**.

Bond	**1**	**2**	**3**
Pd1–C1	1.994(7)	1.968(4)	1.979(2)
Pd1–S1	2.3021(10)	2.2913(9)	2.2970(6)
Pd1–S2	2.3021(10)	2.3040(9)	2.2842(6)
Pd1–Cl1	2.404(2)	2.4284(8)	2.3943(6)
S1–C7	1.836(5)	1.828(4)	1.820(2)
S1–C8	1.775(3)	1.786(4)	1.788(2)
S2–C14	1.836(5)	1.826(4)	1.837(2)
S2–C15	1.775(3)	1.787(4)	1.785(2)
Angle			
C1–Pd1–Cl1	180.00(1)	177.83(10)	179.01(7)
C1–Pd1–S1	85.97(3)	85.28(11)	85.37(7)
C1–Pd1–S2	85.97(3)	85.62(11)	84.91(7)
S1–Pd1–S2	171.94(6)	170.84(3)	170.28(2)
C7–S1–C8	103.7(2)	98.04(17)	104.38(11)
C14–S2–C15	103.7(2)	101.30(17)	103.41(11)

actions between the metalated rings in adjacent molecules at ca. 3.5 Å (see Figure 6). This positive interaction probably compensates any losses derived from steric repulsions that arise as a result of the changing from an *anti* to a *syn* conformation.

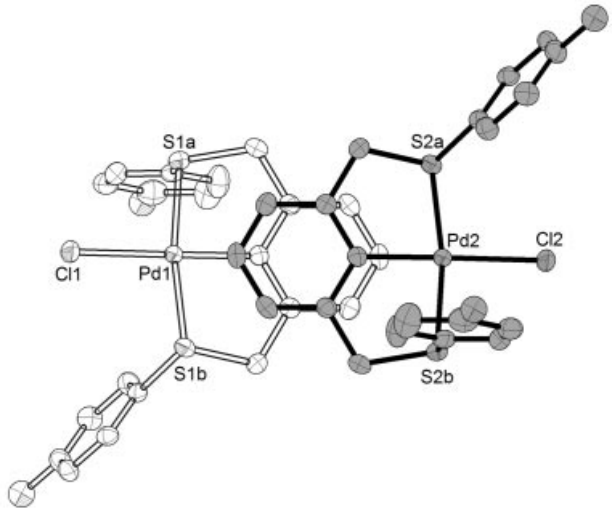


Figure 6. ORTEP drawing of compound **3** showing the aromatic π-stacking interactions between adjacent molecules (hydrogen atoms are omitted for clarity).

The X-ray diffraction molecular structure of compounds [PdCl{SCS–$C_6H_4(CF_3)$-2}] (**4**) and [PdCl{SCS–$C_6H_4(CF_3)$-4}] (**6**) are shown in Figure 7 and Figure 8, respectively and selected bond lengths and angles are reported in Table 3.

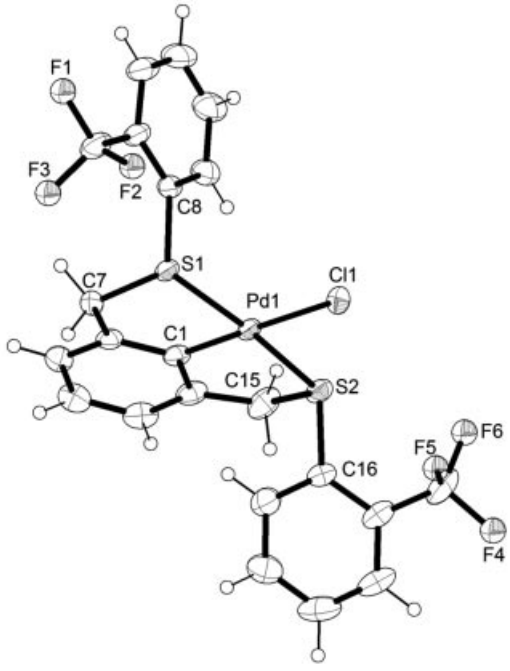


Figure 7. ORTEP drawing of compound [PdCl{SCS–$C_6H_4(CF_3)$-2}] (**4**).

In compounds **4** and **6**, the Pd atoms are also in a slightly distorted square-planar environment: S(1)–Pd(1)–S(2), **4**

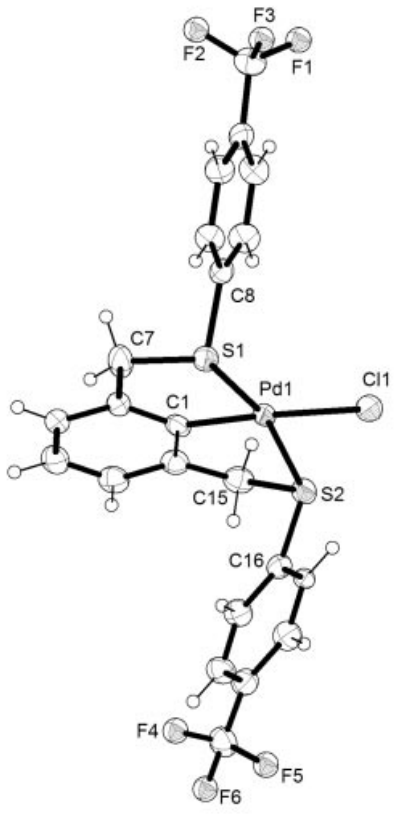


Figure 8. ORTEP drawing of compound [PdCl{SCS–$C_6H_4(CF_3)$-4}] (**6**).

Table 3. Selected bond lengths [Å] and angles [°] with estimated standard deviations for complexes **4** and **6**.

Bond	**4**	**6**
Pd1–C1	1.983(3)	1.982(4)
Pd1–S1	2.3044(13)	2.2767(13)
Pd1–S2	2.2915(12)	2.3195(13)
Pd1–Cl1	2.3893(14)	2.3929(13)
S1–C7	1.830(3)	1.841(5)
S1–C8	1.786(3)	1.787(4)
S2–C15	1.830(3)	1.815(5)
S2–C16	1.792(3)	1.795(5)
Angle		
C1–Pd1–Cl1	178.46(7)	176.82(13)
C1–Pd1–S1	85.47(8)	85.43(14)
C1–Pd1–S2	86.11(8)	85.38(14)
S1–Pd1–S2	171.54(2)	165.99(4)
C7–S1–C8	101.41(12)	101.4(2)
C15–S2–C16	100.07(13)	102.8(2)

171.54(2); **6** 165.99(4)° and Cl(1)–Pd(1)–C(1), **4** 178.46(7); **6** 176.82(13)°. The bonding parameters for Pd are comparable with those observed for complexes **1**–**3** and analogous compounds.[19f,29–31] The $C_6H_4(CF_3)$-*n* (*n* = 2 or 4) groups attached to the metal-bound sulfur atoms are oriented in an *anti* fashion with respect to the square plane, as is the case for **1** and **2**.

Summary and Conclusions

Pincer-type ligands of the SCS class can be prepared with partially fluorinated aromatic substituents. However, only those with a single F or CF_3 group will undergo facile palladation reactions to give the corresponding palladacycle. When the number of F atoms is increased, the resulting electronic effect on the S donor is such that coordination to palladium is too weak to allow for metallation to occur.

The solid-state structures show no unusual steric effects that would prevent these complexes from being used in a variety of catalytic reactions. We are currently testing these complexes as catalysts for the Suzuki coupling of aromatic groups. The results showing the effect of these electron-withdrawing substituted SCS pincers will be reported in due course.

Experimental Section

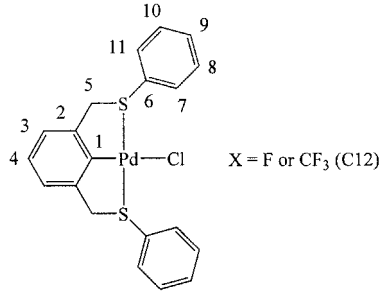
General: All reactions were carried out under inert conditions using conventional Schlenk glassware. The solvents were dried by using established procedures and distilled under nitrogen immediately prior to use. TLC (Merck, 2×5 cm^2 Kieselgel 60 F254) was used to monitor the progress of the reaction under study with hexane/ethyl acetate (9:1) as the eluent. The IR spectra were measured with a Nicolet Avatar FT-IR spectrometer. ^{1}H-, ^{13}C-, and ^{19}F NMR spectra were recorded with a Varian Unity Inova 300 spectrometer operating at 300 MHz. Chemical shifts are relative to TMS $\delta = 0$ (^{1}H, ^{13}C) and $CFCl_3$ $\delta = 0$ (^{19}F) using CD_3CN as the solvent. Electron impact mass spectra were recorded with a Jeol JMSSX102A mass spectrometer. Elemental analyses were determined using a Fisons EA1108 instrument. The starting material 1,3-bis(bromomethyl)benzene was obtained from Aldrich Chemical Co. and used without further purification. C_6H_3-1,3-$(CH_2SC_6F_5)_2$, C_6H_3-1,3-$(CH_2SC_6HF_4$-4$)_2$,[25] and $Pb(SR_f)_2$[32] (R_f = C_6H_4F-2, C_6H_4F-3, and C_6H_4F-4) were prepared according to published procedures.

Preparation of Compounds L1–L6: C_6H_4-1,3-$(CH_2SC_6H_4F$-*n*$)_2$ (**L1**–**L3**) and C_6H_4-1,3-$[CH_2SC_6H_4(CF_3)$-*n*$]_2$ (**L4**–**L6**).

In all reactions, stoichiometric quantities of reactants were used, and since all preparations were similar, only a typical procedure is described.

$Pb(SC_6H_4F$-*n*$)_2$ or $Pb[SC_6H_4(CF_3)$-*n*$]_2$ (0.41 mmol) was added to a mixture of 1,3-bis(bromomethyl)benzene (0.113 g, 0.41 mmol) in acetonitrile (30 mL). The stirred mixture was maintained under reflux for 24 h. After this time, $PbBr_2$ was filtered off, the solvent was removed under vacuum, and the residue purified by column chromatography (silica gel; hexane/ethyl acetate 9:1).

Spectroscopic parameters follow the numbering scheme shown in the following diagram.



C_6H_4-1,3-$(CH_2SC_6H_4F$-2)$_2$ (L1): Colorless oil; yield; 0.141 g, 92%. IR (KBr): $\tilde{\nu}$ = 3030, 2922, 1593, 1472, 1220, 1260 cm^{-1}. EI-MS: *m*/*z* (%) = 358 [M$^+$] (90), 231 (100), 104 (45). ^{1}H NMR (299.69 MHz, CD_3CN): δ = 4.09 (s, 4 H, 5-H), 7.08 (m, 7 H, 3-H, 4-H, 8-H, 11-H), 7.22 (m, 5 H, 1-H, 9-H, 10-H) ppm. $^{13}C\{^1H\}$ NMR (75.36 MHz, CD_3CN): δ = 37.5 (C-5), 116.5 (d, $^2J_{C,F}$ = 22.7 Hz, C-8), 123.7 (d, $^2J_{C,F}$ = 17.7 Hz, C-6), 125.8 (d, $^3J_{C,F}$ = 3.5 Hz, C-11), 128.8 (C-3), 129.6 (C-4), 129.8 (d, $^3J_{C,F}$ = 8.0 Hz, C-9), 130.3 (C-1), 133.2 (d, $^4J_{C,F}$ = 2.9 Hz, C-10), 138.8 (C-2), 162.1 (d, $J_{C,F}$ = 242.6 Hz, C-7) ppm. ^{19}F NMR (281.96 MHz, CD_3CN): δ = –108.89 (m, $^3J_{F,H}$ = 9.59, $^4J_{F,H}$ = 6.99, $^5J_{F,H}$ = 4.82, $^4J_{F,H}$ = 0.13 Hz) ppm.

C_6H_4-1,3-$(CH_2SC_6H_4F$-3)$_2$ (L2): Colorless oil; yield: 0.138 g, 90%. IR (KBr): $\tilde{\nu}$ = 3060, 2923, 1598, 1473, 1263, 1215 cm^{-1}. EI-MS: *m*/*z* (%) = 358 [M$^+$] (75), 231 (100), 104 (65). ^{1}H NMR (299.69 MHz, CD_3CN): δ = 4.15 (s, 4 H, 5-H), 6.90 (m, 2 H, 9-H), 7.05 (m, 4 H, 7-H, 11-H), 7.35 (m, 6 H, 1-H, 3-H, 4-H, 10-H) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_3CN): δ = 38.1 (C-5), 113.8 (d, $^2J_{C,F}$ = 21.5 Hz, C-9), 116.2 (d, $^2J_{C,F}$ = 23.1 Hz, C-7), 125.5 (d, $^4J_{C,F}$ = 3.0 Hz, C-11), 128.9 (C-3), 129.7 (C-4), 130.3 (C-1), 131.6 (d, $^3J_{C,F}$ = 8.5 Hz, C-10), 138.7 (C-2), 140.0 (d, $^3J_{C,F}$ = 8.0 Hz, C-6), 163.8 (d, $J_{C,F}$ = 244.6 Hz, C-8) ppm. ^{19}F NMR (281.96 MHz, CD_3CN): δ = –113.69 (m, $^3J_{F,H}$ = 9.54, $^3J_{F,H}$ = 6.16, $^4J_{F,H}$ = 9.00, $^5J_{F,H}$ = 0.96 Hz) ppm.

C_6H_4-1,3-$(CH_2SC_6H_4F$-4)$_2$ (L3): White microcrystalline powder; yield: 0.145 g, 95%. M.p. 51–52 °C. IR (KBr): $\tilde{\nu}$ = 2918, 1595, 1490, 1239, 822 cm^{-1}. EI-MS: *m*/*z* (%) = 358 [M$^+$] (85), 231 (100), 104 (45). ^{1}H NMR (299.69 MHz, CD_3CN): δ = 4.04 (s, 4 H, 5-H), 7.00 (m, 4 H, 8-H, 10-H), 7.13 (m, 4 H, 1-H, 3-H, 4-H), 7.28 (m, 4 H, 7-H, 11-H) ppm. $^{13}C\{^1H\}$ NMR (75.36 MHz, CD_3CN): δ = 39.8 (C-5), 116.9 (d, $^2J_{C,F}$ = 21.7 Hz, C-8, C-10), 128.7 (C-3), 129.5 (C-1), 130.4 (C-4), 132.1 (d, $^4J_{C,F}$ = 2.8 Hz, C-6), 133.7 (d, $^3J_{C,F}$ = 8.0 Hz, C-7, C-11), 139.1 (C-2), 162.8 (d, $J_{C,F}$ = 244.7 Hz, C-9) ppm. ^{19}F NMR (281.96 MHz, CD_3CN): δ = –114.6 (m, $^4J_{F,H}$ = 5.21, $^3J_{F,H}$ = 9.02 Hz) ppm. $C_{20}H_{16}F_2S_2$ (358.5): calcd. C 67.02, H, 4.50, S 17.86; found C 66.94, H 4.45, S 17.23.

C_6H_4-1,3-$[CH_2SC_6H_4(CF_3)$-2$]_2$ (L4): Yellowish oil; yield: 0.158 g, 80.4%. IR (KBr): $\tilde{\nu}$ = 1312, 1112, 1172, 1034, 760, 1258, 1440, 1592 cm^{-1}. EI-MS: *m*/*z* (%) = 458 [M$^+$] (40), 281 (100), 104 (30). ^{1}H NMR (299.69 MHz, CD_3CN): δ = 4.20 (s, 4 H, 5-H), 7.22 (m, 3 H, 3-H, 4-H), 7.32 (m, 3 H, 1-H, 9-H), 7.48 (m, 4 H, 10-H, 11-H), 7.66 (m, 2 H, 8-H) ppm. $^{13}C\{^1H\}$ NMR (75.36 MHz, CD_3CN): δ = 38.8 (C-5), 127.3 (C-9), 127.8 (q, $^3J_{C,F}$ = 5.8 Hz, C-8), 129.1 (C-3), 129.8 (C-4), 130.6 (C-1), 132.2 (C-11), 133.5 (C-10), 136.6 (C-6), 138.2 (C-2), 129.6 (q, $^2J_{C,F}$ = 30.2 Hz, C-7), 125.2 (q, $J_{C,F}$ = 273.4 Hz, C-12) ppm. ^{19}F NMR (281.96 MHz, CD_3CN): δ = –56.56 ppm.

C_6H_4-1,3-$[CH_2SC_6H_4(CF_3)$-3$]_2$ (L5): Yellowish oil; yield: 0.155 g,79.3%. IR (KBr): $\tilde{\nu}$ = 1322, 1124, 1165, 1072, 695, 793, 711, 1425 cm^{-1}. EI-MS: *m*/*z* (%) = 458 [M$^+$] (20), 281 (75), 104 (70). ^{1}H NMR (299.69 MHz, CD_3CN): δ = 4.18 (s, 4 H, 5-H), 7.28 (m, 3 H, 3-H, 4-H), 7.33 (m, 1 H, 1-H), 7.48 (m, 8 H, 7-H, 9-H, 10-H, 11-H) ppm. $^{13}C\{^1H\}$ NMR (75.36 MHz, CD_3CN): δ = 38.1 (C-5), 123.7 (q, $^3J_{C,F}$ = 4.0 Hz, C-9), 126.1 (q, $^3J_{C,F}$ = 3.7 Hz, C-7), 128.9 (C-3), 129.7 (C-4), 130.8 (C-1), 133.7 (C-10), 133.4 (C-11), 138.6 (C-2), 139.1 (C-6), 131.5 (q, $^2J_{C,F}$ = 32.3 Hz, C-8), 125.1 (q, $J_{C,F}$ = 272.4 Hz, C-12) ppm. ^{19}F NMR (281.96 MHz, CD_3CN): δ = –62.99 ppm.

C_6H_4-1,3-$[CH_2SC_6H_4(CF_3)$-4$]_2$ (L6): White microcrystalline powder; yield: 0.166 g, 85%. M.p. 61–63 °C. IR (KBr): $\tilde{\nu}$ = 1327, 1121, 1095, 1063, 1164, 1605, 823, 1013 cm^{-1}. EI-MS: *m*/*z* (%) = 458 [M$^+$] (30), 281 (100), 104 (25). ^{1}H NMR (299.69 MHz, CD_3CN): δ = 4.21 (s, 4 H, 5-H), 7.26 (m, 3 H, 3-H, 4-H), 7.40 (m, 5 H, 1-H, 8-H, 10-H), 7.52 (m, 4 H, 7-H, 11-H) ppm. $^{13}C\{^1H\}$ NMR (75.36 MHz, CD_3CN): δ = 37.3 (C-5), 129.0 (C-3), 129.9 (C-4), 130.4 (C-1), 138.4 (C-2), 143.5 (C-6), 126.6 (q, $^3J_{C,F}$ = 7.9 Hz, C-8, C-10), 128.7 (C-7, C-11), 125.5 (q, $J_{C,F}$ = 271.3 Hz, C-12), 127.9 (q, $^2J_{C,F}$ = 32.3 Hz, C-9) ppm. ^{19}F NMR (281.96 MHz, CD_3CN): δ = –62.60 ppm.

General Procedure for the Preparation of Palladium(II) Complexes 1–6: Dichloropalladium(II) (0.216 g, 1.22 mmol) in acetonitrile (25 mL) was heated under reflux for 1 h. Silver tetrafluoroborate (0.495 g, 2.54 mmol) was added to this solution. Silver chloride was separated from the suspension by filtration through Celite. The ligand (**L1**–**L6**) (0.435 g, 1.22 mmol) was dissolved in warm acetonitrile (10 mL) and added to the filtrate. The solution immediately turned orange and was heated under reflux for 4 h. The reaction mixture turned yellow, and excess NaCl (0.189 g, 3.23 mmol) was added. The suspension was stirred overnight. The yellow precipitate was filtered off and washed three times with water and two times with ethanol. The products were obtained as yellow powders.

[PdCl{C_6H_3-1,3-$(CH_2SC_6H_4F$-2)$_2$}] (1): Yellow crystals; yield: 0.583 g, 96%. M.p. 187 °C. IR (KBr): $\tilde{\nu}$ = 750, 1470, 1449, 1221, 1262, 724, 818, 1061, 1029, 2900, 2976, 3046 cm^{-1}. EI-MS: *m*/*z* (%) = 500 [M + 1]$^+$ (5), 463 (60), 391 (40). ^{1}H NMR (299.69 MHz, $CDCl_3$): δ = 4.65 (s, 4 H, 5-H), 7.18 (m, 4 H, 8-H, 11-H), 6.97 (m, 3 H, 3-H, 4-H), 7.45 (m, 2 H, 9-H), 8.28 (m, 2 H, 10-H) ppm. $^{13}C\{^1H\}$ NMR (75.36 MHz, $CDCl_3$): δ = 52.1 (C-5), 116.5 (d, $^2J_{C,F}$ = 21.7 Hz, C-8), 119.0 (d, $^2J_{C,F}$ = 16.1 Hz, C-6), 122.2 (C-3), 123.0 (d, $^3J_{C,F}$ = 8.2 Hz, C-9), 125.1 (d, $^3J_{C,F}$ = 3.8 Hz, C-11), 125.2 (C-4), 136.5 (C-10), 148.4 (C-2), 159.2 (C-1), 160.8 (d, $J_{C,F}$ = 251.1 Hz, C-7) ppm. ^{19}F NMR (281.96 MHz, $CDCl_3$): δ = –106.31 ppm. $C_{20}H_{15}S_2F_2PdCl$ (499.3): calcd. C 48.11, H 3.03, S 12.84; found: C 48.30, H 3.36, S 13.01.

[PdCl{C_6H_3-1,3-$(CH_2SC_6H_4F$-3)$_2$}] (2): Yellow crystals; yield: 0.492 g, 81%. M.p. 165 °C. IR (KBr): $\tilde{\nu}$ = 727, 1472, 1214, 873, 1579, 749, 777, 1420, 674, 1264, 2922, 3053 cm^{-1}. EI-MS: *m*/*z* (%) = 500 [M + 1]$^+$ (5), 463 (70). ^{1}H NMR (299.69 MHz, $CDCl_3$): δ = 4.62 (s, 4 H, 5-H), 7.04 (m, 5 H, 9-H, 3-H, 4-H), 7.34 (m, 2 H, 10-H), 7.51 (m, 2 H, 7-H), 7.61 (m, 2 H, 11-H) ppm. $^{13}C\{^1H\}$ NMR (75.36 MHz, $CDCl_3$): δ = 51.2 (C-5), 117.0 (d, $^2J_{C,F}$ = 21.2 Hz, C-9), 118.0 (d, $^2J_{C,F}$ = 24.2 Hz, C-7), 122.5 (C-3), 125.19 (C-4), 126.9 (d, $^4J_{C,F}$ = 3.0 Hz, C-11), 131.1 (d, $^3J_{C,F}$ = 8.1 Hz, C-10), 133.7 (d, $^3J_{C,F}$ = 8.0 Hz, C-6), 149.0 (C-2), 161.0 (C-1), 162. 5 (d, $J_{C,F}$ = 251.6 Hz, C-8) ppm. ^{19}F NMR (281.96 MHz, $CDCl_3$): δ = –109.8 ppm. $C_{20}H_{15}S_2F_2PdCl$ (499.3): calcd. C 48.11, H 3.03, S 12.84; found C 48.05, H 3.17, S 13.01.

[PdCl{C_6H_3-1,3-$(CH_2SC_6H_4F$-4)$_2$}] (3): Yellow crystals; yield: 0.413 g, 68%. M.p. 198 °C. IR (KBr): $\tilde{\nu}$ = 1489, 1218, 1153, 826, 816, 843, 1415, 772, 3058, 298, 3085 cm^{-1}. EI-MS: *m*/*z* (%) = 500 [M + 1]$^+$ (10), 463 (100). ^{1}H NMR (299.69 MHz, $CDCl_3$): δ = 4.67 (s, 4 H, 5-H), 7.00 (m, 3 H, 3-H, 4-H), 7.186 (m, 4 H, 8-H, 10-H), 7.94 (m, 4 H, 7-H, 11-H) ppm. $^{13}C\{^1H\}$ NMR (75.36 MHz, $CDCl_3$): δ = 53.0 (C-5), 117.6 (d, $^2J_{C,F}$ = 22.8 Hz, C-8, C-10), 123.5 (C-3), 126.0 (C-4), 129.0 (d, $^4J_{C,F}$ = 3.0 Hz, C-6), 135.3 (d, $^3J_{C,F}$ = 9.1 Hz, C-7, C-11), 150.6 (C-2), 163.1 (C-1), 164.5 (d, $J_{C,F}$ = 248.1 Hz, C-9) ppm. ^{19}F NMR (281.96 MHz, $CDCl_3$): δ = –107.1 ppm. $C_{20}H_{15}S_2F_2PdCl$ (499.3): calcd. C 48.11, H 3.03, S 12.84; found C 44.90, H 3.03, S 12.27.

[PdCl{SCS–$C_6H_4(CF_3)$-2}] (4): Yellow crystals; yield: 0.450 g, 79%. M.p. 130 °C (dec). IR (KBr): $\tilde{\nu}$ = 1310, 1181, 1117, 1029, 770, 1092, 1265 cm^{-1}. ^{1}H NMR (299.69 MHz, $CDCl_3$): δ = 4.54 (s, 4 H, 5-H), 7.03 (m, 3 H, 3-H, 4-H), 7.69 (m, 6 H, 8-H, 9-H, 11-H), 8.75 (m, 2 H, 10-H) ppm. $^{13}C\{^1H\}$ NMR (75.36 MHz, $CDCl_3$): δ = 55.7 (C-

Table 4. Crystallographic data, solution and refinement parameters for single crystal structure determinations of compounds **L3**, **1**, **2**, **3**, **4**, and **6**.

	L3	**1**	**2**	**3**	**4**	**6**
Formula	$C_{20}H_{16}F_2S_2$	$C_{20}H_{15}ClF_2PdS_2$	$C_{20}H_{15}ClF_2PdS_2$	$C_{20}H_{15}ClF_2PdS_2$	$C_{22}H_{15}ClF_6PdS_2$	$C_{22}H_{15}ClF_6PdS_2$
Formula mass	358.47	499.29	499.29	499.29	599.31	599.31
Crystal system	orthorhombic	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic
Space group	*P*nma	*F*dd2	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/c$
T [K]	298(2)	298(2)	173(2)	173(2)	173(2)	173(2)
a [Å]	6.868(5)	35.219(5)	8.5669(5)	9.2552(11)	17.173(12)	8.371(3)
b [Å]	33.026(5)	9.817(5)	9.5228(6)	18.417(2)	8.809(6)	27.069(8)
c [Å]	7.623(5)	10.920(5)	11.8512(7)	11.2976(13)	14.689(10)	9.899(3)
α [°]			96.153(1)			
β [°]			100.303(1)	103.993(1)	98.143(7)	107.945(3)
γ [°]			103.385(1)			
V [Å^3]	1729.1(2)	3776(3)	914.2(1)	1868.6(4)	2200(3)	2134.0(1)
Z	8	8	2	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.377	1.757	1.814	1.775	1.810	1.865
μ [mm^{-1}]	0.325	1.365	1.410	1.380	1.214	1.251
reflections collected	3154	1813	7260	17746	19198	20216
unique reflections	2331	1580	3201	3291	3880	3752
R_1/R_2w $[I > 2\sigma(I)]$[a]	0.0532/0.0978	0.0270/0.0604	0.0329/0.0971	0.0207/0.0595	0.0246/0.0712	0.0442/0.1057
R_1/R_2w (all data)[b]	0.1391/0.1229	0.0322/0.0622	0.0335/0.0976	0.245/0.0619	0.0275/0.0770	0.0474/0.1078
GoF on F^2	0.954	1.066	1.089	1.026	1.085	1.088
Parameters/restrains	112/0	120/1	235/0	235/0	289/0	289/0
Min./max. residual density [e Å^{-3}]	0.275/0.259	–0.390/0.376	–1.13/1.41	–0.22/0.40	–0.52/0.55	–1.31/1.66

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$;. [b] $R_2w = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$, where $w = q[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$.

5), 122.4 (C-3), 125.0 (C-4), 125.6 (C-9), 126.9 (C-8), 131.3 (C-11), 133.5 (C-10), 147.8 (C-2) ppm. ^{19}F NMR (281.96 MHz, $CDCl_3$): δ = –59.09 ppm.

[PdCl{SCS–C$_6$H$_4$(CF$_3$)-3}] (5): Yellow crystals; yield: 0.205 g, 36%. M.p. 194 °C. IR (KBr): $\tilde{\nu}$ = 1320, 1122, 1176, 1103, 1072, 692, 797, 769 cm^{-1}. FAB(+)-MS: *m*/*z* (%) = 598 [M$^+$] (2), 563 (100), 417 (10), 385 (8), 279 (20), 135 (10). ^{1}H NMR (299.69 MHz, $CDCl_3$): δ = 4.67 (s, 4 H, 5-H), 7.05 (m, 3 H, 3-H, 4-H), 7.53 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, 10-H), 7.65 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, 9-H), 8.00 (s, 2 H, 7-H), 8.13 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, 11-H) ppm. ^{13}C{^{1}H} NMR (75.36 MHz, $CDCl_3$): δ = 51.6 (C-5), 122.6 (C-3), 123.2 (q, $J_{C,F}$ = 273.2 Hz, C-12), 125.4 (C-4), 126.8 (q, $^3J_{C,F}$ = 3.7 Hz, C-9), 127.5 (q, $^3J_{C,F}$ = 3.7 Hz, C-7), 130.3 (C-10), 132.0 (q, $^2J_{C,F}$ = 33.2 Hz, C-8), 133.3 (C-6), 135.2 (C-11), 148.6 (C-2), 160.7 (C-1) ppm. ^{19}F NMR (281.96 MHz, $CDCl_3$): δ = –63.16 ppm. $C_{22}H_{15}F_6S_2PdCl$ (599.3): calcd. C 44.09, H 2.52, S 10.7; found C 43.80, H 2.72, S 11.28.

[PdCl{SCS–C$_6$H$_4$(CF$_3$)-4}] (6): Yellow crystals; yield: 0.251 g, 44%. M.p. 230 °C. IR (KBr): $\tilde{\nu}$ = 1320, 1123, 1061, 1169, 1085, 1011, 838, 1604 cm^{-1}. FAB(+)-MS: *m*/*z* (%) = 598 [M$^+$] (2), 563 (100), 417 (10), 385 (8), 279 (25), 135 (10). ^{1}H NMR (299.69 MHz, $CDCl_3$): δ = 4.66 (s, 4 H, 5-H), 7.07 (m, 3 H, 3-H, 3-H), 7.62 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H, 8-H, 10-H), 7.91 (d, $^3J_{H,H}$ = 8.1 Hz, 4 H, 7-H7, 11-H) ppm. ^{13}C{^{1}H} NMR (75.36 MHz, $CDCl_3$): δ = 50.3 (C-5), 122.7 (C-3), 123.4 (q, $J_{C,F}$ = 270.8 Hz, C-12), 125.4 (C-4), 126.6 (q, $^3J_{C,F}$ = 3.6 Hz, C-10, C-8), 128.8 (C-6), 130.8 (C-7, C-11), 131.6 (q, $^2J_{C,F}$ = 33.2 Hz, C-9), 148.8 (C-2), 161.3 (C-1) ppm. ^{19}F NMR (281.96 MHz, $CDCl_3$): δ = –63.40 ppm.

Crystal Data: Crystallographic data, solution and refinement parameters for the single crystal structure determinations of compounds **L3**, **1**, **2**, **3**, **4**, and **6** are reported in Table 4. Single crystals of all compounds were obtained from slow evaporation of saturated acetonitrile solutions. X-ray diffraction data for compounds **L3** and **1** were collected at 298 K with a Siemens P4 automatic diffractometer and analyzed using graphite-monochromated Mo-K_α X-ray radiation (λ = 0.71073 Å). X-ray diffraction data for compounds **2**, **3**, **4**, and **6** were collected at 173 K with a Bruker APEX CCD single crystal diffractometer with Mo-K_α X-ray radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS 97–2.[33] Least-squares refinement based on F^2 was carried out by a full-matrix method with SHELXL 97–2.[33] All non-hydrogen atoms were refined with anisotropic thermal parameters. The location of hydrogen atoms was generated geometrically and included in the refinement with an isotropic fixed thermal parameter using a "riding" model. Neutral atom scattering factors and anomalous dispersion corrections were taken from International Tables for Crystallography.[34] Molecular structure drawings were generated using ORTEP3 for Windows.[35]

CCDC-251029 (**L3**), -251028 (**1**), -254754 (**2**), -281816 (**3**), -281832 (**4**), and -281831 (**6**) 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.

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