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# Allyl-palladium compounds with fluorinated benzenethiolate ligands. X-ray crystal structure of $[(\eta^3-C_3H_5)Pd(\mu-SC_6H_4F-4)_2Pd(\eta^3-C_3H_5)]$

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### Abstract

Treatment of the di- $\mu$ -chloride allyl-palladium complex [( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Pd( $\mu$ -Cl)<sub>2</sub>Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)] with Pb(SR)<sub>2</sub> in acetone affords dinuclear fluorothiolate bridged complexes of the type [( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Pd( $\mu$ -SR)<sub>2</sub>Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)] (R = C<sub>6</sub>F<sub>5</sub>, 1; C<sub>6</sub>HF<sub>4</sub>-4, 2; C<sub>6</sub>H<sub>4</sub>F-2, 3; C<sub>6</sub>H<sub>4</sub>F-3, 4 and C<sub>6</sub>H<sub>4</sub>F-4, 5). Complex 1 reacts with *para*-substituted phosphines P(C<sub>6</sub>H<sub>4</sub>X-4)<sub>3</sub> to give the mononuclear perfluorobenzenethiolate complexes [Pd(SC<sub>6</sub>F<sub>5</sub>)( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(P(C<sub>6</sub>H<sub>4</sub>X-4)<sub>3</sub>)] (X = F, 6; CF<sub>3</sub>, 7; OCH<sub>3</sub>, 8 and CH<sub>3</sub>, 9). The single crystal X-ray diffraction structure of [( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Pd( $\mu$ -SC<sub>6</sub>H<sub>4</sub>F-4)<sub>2</sub>Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)] (5) has been resolved. © 2001 Published by Elsevier Science Ltd.

Keywords: Palladium; Fluorothiolate; Allyl; NMR spectroscopy; Crystal structures

### 1. Introduction

The role of  $\eta^3$ -allyl–palladium compounds in several palladium-catalysed organic syntheses is now well established [1]. Reviews focused on reactions such as carbonyl allylation [2], carbonylation [3], allyl alkylation [4], decarbopalladation [5] or on their application as enantioselective homogeneous catalysts [6] have been published.

In contrast with other derivatives of allyl-palladium complexes [1], those bearing sulfur-containing ligands are relatively scarce [7–11], even though species with the fragment [Pd(SR)( $\eta^3$ -allyl)] are potential precursors of compounds with an organic-SR skeleton and, indeed, [Pd(SR)( $\eta^3$ -allyl-R')L] affords R'CH=CHCH<sub>2</sub>SR [9].

As part of our continued interest in dinuclear compounds with fluoroarylthiolato bridging units [12], we have studied a series of allyl-palladium dinuclear complexes,  $[(\eta^3-C_3H_5)Pd(\mu-SR)_2Pd(\eta^3-C_3H_5)]$  (R = fluorinated substituents), and the reactivity of  $[(\eta^3-C_3H_5)-Pd(\mu-SC_6F_5)_2Pd(\eta^3-C_3H_5)]$  towards *para*-substituted phosphines. To the best of our knowledge, fluorothiolate-containing derivatives of allyl complexes are represented by a single example:  $[(\eta^3-C_3H_5)Ni(\mu-SC_6F_5)_2-Ni(\eta^3-C_3H_5)]$  [10].

In this paper we discuss the synthesis and properties of  $[(\eta^3-C_3H_5)Pd(\mu-SR)_2Pd(\eta^3-C_3H_5)]$  (R = C<sub>6</sub>F<sub>5</sub>, 1; C<sub>6</sub>HF<sub>4</sub>-4, 2; C<sub>6</sub>H<sub>4</sub>F-2, 3; C<sub>6</sub>H<sub>4</sub>F-3, 4 and C<sub>6</sub>H<sub>4</sub>F-4, 5) and [Pd(SC<sub>6</sub>F<sub>5</sub>)(\eta^3-C\_3H\_5)(P(C<sub>6</sub>H<sub>4</sub>X-4)<sub>3</sub>)] (X = F, 6; CF<sub>3</sub>, 7; OCH<sub>3</sub>, 8 and CH<sub>3</sub> 9) and the single crystal X-ray diffraction structure of compound 5.

### 2. Experimental

All manipulations were carried out under dry, oxygen-free dinitrogen atmospheres using standard vacuum and Schlenk-tube techniques.

Solvents were dried and degassed using standard techniques [13], and thin layer chromatography (TLC)

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(Merck,  $5 \times 7.5$  cm<sup>2</sup> Kieselgel 60 F<sub>254</sub>) was used when possible to monitor the progress of the reaction under study.

<sup>1</sup>H, <sup>19</sup>F $\{^{1}H\}$  and <sup>31</sup>P $\{^{1}H\}$  NMR spectra were recorded on a Varian-360 spectrometer operating at 360.006, 338.70 and 145.76 MHz, respectively. Proton spectra are referenced internally using the residual protio solvent resonance relative to SiMe<sub>4</sub> ( $\delta = 0$ ), <sup>19</sup>F externally to CFCl<sub>3</sub> ( $\delta = 0$ ) and <sup>31</sup>P externally to 85%  $H_3PO_4$  ( $\delta = 0$ ) using the high frequency positive convention. All chemical shifts ( $\delta$ ) are quoted in ppm and coupling constants (J) in Hz. Positive-ion FAB mass spectra were recorded on a JEOL SX102 mass spectrometer operated at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol 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.

Elemental analyses were performed by Galbraith Laboratories Inc., USA.

 $[(\eta^3-C_3H_5)Pd(\mu-Cl)_2Pd(\eta^3-C_3H_5)]$  [14] and Pb(SR)<sub>2</sub> [15,16] were prepared according to published methods. All other materials were used as commercially supplied.

2.1. Preparation of complexes  $[(\eta^{3}-C_{3}H_{5})Pd(\mu-SR)_{2}Pd(\eta^{3}-C_{3}H_{5})]$  ( $R = C_{6}F_{5}$ , **1**;  $C_{6}HF_{4}$ -4, **2**;  $C_{6}H_{4}F$ -2, **3**;  $C_{6}H_{4}F$ -3, **4** and  $C_{6}H_{4}F$ -4, **5**)

 $[(\eta^3-C_3H_5)Pd(\mu-Cl)_2Pd(\eta^3-C_3H_5)]$  (0.5 g, 1.37 mmol) and Pb(SR)<sub>2</sub> (1.37 mmol) were dissolved in 60 ml of acetone and the resulting yellow solution was magnetically stirred for 2 h. PbCl<sub>2</sub> was filtered off and the resulting clear solutions were dried under vacuum. The yellow solids were dissolved in 15 ml of acetone and slow evaporation of these solutions at room temperature afforded yellow crystals of compounds 1–5.

# 2.1.1. $[(\eta^{3}-C_{3}H_{5})Pd(\mu-SC_{6}F_{5})_{2}Pd(\eta^{3}-C_{3}H_{5})]$ (1)

Yellow, yield 75%, m.p. 172 °C (dec). *Anal.* Found: C, 30.8; H, 1.1; S, 9.7. Calc. for  $C_{18}H_{10}F_{10}Pd_2S_2$ : C, 31.2; H, 1.5; S, 9.3%. MS, m/z calc.: 693, found: 693.

### 2.1.2. $[(\eta^{3}-C_{3}H_{5})Pd(\mu-SC_{6}HF_{4}-4)_{2}Pd(\eta^{3}-C_{3}H_{5})]$ (2)

Yellow, yield 87%, m.p. 145 °C (turns green), 180 °C (dec). *Anal.* Found: C, 32.3; H, 1.8; S, 9.7. Calc. for  $C_{18}H_{12}F_8Pd_2S_2$ : C, 32.9; H, 1.8; S, 9.8%. MS, *m/z* calc.: 657, found: 657.

# 2.1.3. $[(\eta^{3}-C_{3}H_{5})Pd(\mu-SC_{6}H_{4}F-2)_{2}Pd(\eta^{3}-C_{3}H_{5})]$ (3)

Yellow, yield 95%, m.p. 112 °C (turns green), 122 °C (dec). *Anal.* Found: C, 38.1; H, 3.4; S, 10.1. Calc. for  $C_{18}H_{18}F_2Pd_2S_2$ : C, 39.4; H, 3.3; S, 11.7%. MS, m/z calc.: 549, found: 549.

# 2.1.4. $[(\eta^{3}-C_{3}H_{5})Pd(\mu-SC_{6}H_{4}F-3)_{2}Pd(\eta^{3}-C_{3}H_{5})]$ (4)

Yellow, yield 90%, m.p. 90 °C (turns green), 108 °C (dec). *Anal.* Found: C, 38.4; H, 3.4; S, 10.5. Calc. for  $C_{18}H_{18}F_2Pd_2S_2$ : C, 39.4; H, 3.3; S, 11.7%. MS, m/z calc.: 549, found: 549.

### 2.1.5. $[(\eta^{3}-C_{3}H_{5})Pd(\mu-SC_{6}H_{4}F-4)_{2}Pd(\eta^{3}-C_{3}H_{5})]$ (5)

Yellow, yield 97%, m.p. 93 °C (turns green), 113 °C (dec). *Anal.* Found: C, 38.9; H, 3.5; S, 10.6. Calc. for  $C_{18}H_{18}F_2Pd_2S_2$ : C, 39.4; H, 3.3; S, 11.7%. MS, m/z calc.: 549, found: 549.

# 2.2. Preparation of complexes

 $[Pd(\mu - SC_6F_5)(\eta^3 - C_3H_5)(P(C_6H_4X - 4)_3)]$  (X = F, **6**; CF<sub>3</sub>, 7; CH<sub>3</sub>, **8**; and OCH<sub>3</sub>, **9**)

 $[(\eta^3-C_3H_5)Pd(\mu-SC_6F_5)_2Pd(\eta^3-C_3H_5)]$  (0.2 g, 0.29 mmol) and P(C<sub>6</sub>H<sub>4</sub>X-4)<sub>3</sub> (0.29 mmol) were dissolved in 25 ml of acetone and the resulting yellow solution was magnetically stirred for 2 h and dried under vacuum. The yellow solids were dissolved in 15 ml of acetone and slow evaporation of these solutions at room temperature afforded yellow crystals of compounds **6–9**.

# 2.2.1. $[Pd(SC_6F_5)(\eta^3-C_3H_5)(P(C_6H_4F-4)_3)]$ (6)

Yellow, yield 80%, m.p. 108 °C (dec). *Anal.* Found: C, 47.5; H, 2.0; S, 4.7. Calc. for  $C_{27}H_{17}F_8PPdS$ : C, 48.9; H, 2.6; S, 4.8%. MS, m/z calc.: 662, found: 662.

# 2.2.2. $[Pd(SC_6F_5)(\eta^3 - C_3H_5)(P(C_6H_4(CF_3) - 4)_3)]$ (7)

Yellow, yield 81%, m.p. 111 °C (dec). *Anal.* Found: C, 43.3; H, 1.9; S, 3.5. Calc. for  $C_{30}H_{17}F_{14}PPdS$ : C, 44.3; H, 2.1; S, 3.9%. MS, m/z calc.: 812, found: 812.

2.2.3.  $[Pd(SC_6F_5)(\eta^3-C_3H_5)(P(C_6H_4(OCH_3)-4)_3)]$  (8)

Yellow, yield 90%, m.p. 107 °C (dec). *Anal.* Found: C, 51.0; H, 3.4; S, 4.1. Calc. for  $C_{30}H_{26}F_5O_3PPdS$ : C, 51.6; H, 3.8; S, 4.6%. MS, m/z calc.: 699, found: 699.

# 2.2.4. $[Pd(SC_6F_5)(\eta^3-C_3H_5)(P(C_6H_4(CH_3)-4)_3)]$ (9)

Yellow, yield 95%, m.p. 108 °C (dec). *Anal.* Found: C, 55.1; H, 3.9; S, 4.6. Calc. for  $C_{30}H_{26}F_5PPdS$ : C, 55.4; H, 4.0; S, 4.9%. MS, m/z calc.: 651, found: 651.

### 2.3. Single-crystal X-ray structure analysis

Crystallographic data for compound 5 are listed in Table 1. Intensities were collected using graphite monochromatised Mo K $\alpha$  radiation in a Siemens P4/ PC diffractometer using  $\omega - 2\theta$  scans at variable scan speeds and were corrected for Lp effects. Absorption corrections were not considered as necessary, due to the thin needle shape of the crystal. The structure was solved by interpretation of Patterson maps [17,18] and anisotropically refined.

After full anisotropic refinement, large thermal parameters of the central carbon atoms of the allyl groups and peaks remaining in this vicinity suggested that the allyl groups were disordered. The occupancy of the central carbons was refined yielding a value near 50% and peaks corresponding to the alternate positions of these carbons were added.

This model was successfully refined including anisotropic thermal parameters for the half carbon atoms. The final model features 50/50 disordered central allyl carbons atoms, two sets of half hydrogen atoms, and a single position for the terminal carbon atoms. The disordered model produced only a slightly lower *R*value. However, the disordered model does account for the largest peaks in the difference map and also yields smaller thermal parameters, indicating that the disordered model is better.

The hydrogen atoms were placed in calculated positions. The weighting scheme gave satisfactory agreement analyses.

Table 1

Crystal data and details of the structure determination for  $[{Pd(\mu-SC_6H_4F-4)(\eta^3-allyl)}_2]$  (5)

Crystal data	
Empirical formula	$C_{18}H_{18}F_2Pd_2S_2$
Formula weight	549.30
Crystal system	orthorhombic
Space group	Pnma (No. 62)
a (Å)	9.040(2)
b (Å)	20.639(2)
c (Å)	10.1150(10)
α (°)	90
β (°)	90
γ (°)	90
V (Å <sup>3</sup> )	1887.2(5)
Ζ	4
$D_{\rm obs}, D_{\rm calc} \ ({\rm g \ cm^{-3}})$	0.000, 1.933
F(000)	1072
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	2.1
Crystal size (mm)	$0.7 \times 0.1 \times 0.1$
Data collection	
Temperature (K)	293
Radiation (Å)	Mo Kα 0.71073
$\theta$ Range (°)	2.2-30.0
Scan (type and range) (°)	$0.00 + 0.35 \operatorname{Tan}(\theta)$
Reference reflection(s)	
Dataset	-1: 12 -29: 1;
	-1:14
Total, unique data, $R_{int}$	3632, 2822, 0.036
Observed data $[I > 2.0\sigma(I)]$	1975
Refinement	
$N_{\rm ref}, N_{\rm par}$	2822, 122
R, wR, S	0.0424, 0.0991, 0.99
$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2 + 0.4713P]$ where $A$	$P = (F_{\rm o}^2 + 2F_{\rm c}^2)/3$
Maximum and average shift/error	0.04, 0.00
Minimum and maximum resd. dens.	-0.63, 0.86
$(e Å^{-3})$	

#### 3. Results and discussion

Yields,  $FAB^+$  MS, melting points and analytical data consistent with the given formulae for compounds 1-9 are shown in Section 2. Apart from the expected characteristic absorptions corresponding to the fluorinated or the allylic moieties [14–16], the IR spectra do not show any unusual features.

NMR data for compounds 1-5 are collected in Table 2, and those corresponding to compounds 6-9 are shown in Table 3. <sup>1</sup>H and <sup>19</sup>F{<sup>1</sup>H} NMR spectra have been simulated using gNMR-3 [19]. As expected, experimental <sup>31</sup>P{<sup>1</sup>H} NMR spectra exhibit single absorptions only. The numbering used to denote the nuclei is shown in Scheme 1.

# 3.1. Dinuclear complexes

Metathetical reaction of the palladium complex [ $(\eta^3-C_3H_5)Pd(\mu-Cl)_2Pd(\eta^3-C_3H_5)$ ] with the anionic pseudohalogens (SR)<sup>-</sup> (R = C\_6F\_5, C\_6HF\_4-4, C\_6H\_4F-2, C\_6H\_4F-3 and C\_6H\_4F-4) in acetone solutions allows the preparation of the corresponding fluorothiolate-bridged compounds [ $(\eta^3-C_3H_5)Pd(\mu-SR)_2Pd(\eta^3-C_3H_5)$ ] (R = C\_6F\_5, 1; C\_6HF\_4-4, 2; C\_6H\_4F-2, 3; C\_6H\_4F-3, 4 and C\_6H\_4F-4, 5), as shown in Reaction (1).

 $[(\eta^{3}-C_{3}H_{5})Pd(\mu-Cl)_{2}Pd(\eta^{3}-C_{3}H_{5})] + Pb(SR)_{2} - --- [(\eta^{3}-C_{3}H_{5})Pd(\mu-SR)_{2}Pd(\eta^{3}-C_{3}H_{5})] + PbCb_{2}$ 

R	
C <sub>6</sub> F <sub>5</sub>	
C6HF4-4	(1)
C6H4F-2	( )
C6H4F-3	
C <sub>6</sub> H <sub>4</sub> F-4	
	R C6F5 C6HF4-4 C6H4F-2 C6H4F-3 C6H4F-4

Compounds 1-5 are yellow, diamagnetic, crystalline solids that are soluble in acetone and dichloromethane. All complexes are relatively stable in the solid state although their solutions darken and eventually turn black after 2-3 months. On heating, complexes 2-5 develop a green colour before reaching their decomposition temperature. These transitions have not been investigated further.

The <sup>1</sup>H NMR spectra of the dinuclear complexes 1-5 (Table 2) at room temperature exhibit only one set of resonances for the allyl group, i.e. three resonances with the expected intensity ratio of 1:2:2. The assignments of the Hb and Ha protons on the allyl ligand (Scheme 1) were based upon their coupling with Ha, since the *anti*-periplanar Hc should have a larger coupling constant (11–17 Hz) than the *syn*-periplanar Hb proton (6–8 Hz). Geminal coupling between the Hb and Hc protons is not observed and so this coupling constant must be small (<1 Hz). Small geminal coupling constants have been reported for other allyl–metal complexes [10].

The shielding order for the allylic protons is  $\delta Hb > \delta Hc > \delta Ha$ , and while  $\delta Ha$  and  $\delta Hc$  span a range of

#### Table 2

NMR data of [(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)Pd(μ-SR)<sub>2</sub>Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)] (1-5), at 298 K

Compound	Ligand			
	Nucleus		$\delta$ (ppm)	J (Hz)
$1 [{Pd(\mu-SC_6F_5)(\eta^3-C_3H_5)}_2]$	allyl	На	5.58 (2H, tt)	$J_{\text{Ha-Hb}} = 7.2, \ J_{\text{Ha-Hc}} = 14.4$
		Hb	3.81 (4H, d)	$J_{\mathrm{Hb-Hc}}\!<\!1$
		Hc	3.03 (4H, d)	
	SR	F2,6	-132.97 <sup>a</sup> (4F, m)	$J_{F2,6-F3,5} = 22.9,$ $J_{F2,6-F4} = 2.5$
		F4	-162.77 <sup>a</sup> (2F, tt)	$J_{\text{F4}-\text{F3},5} = 20.7$
		F3,5	-165.27  a (4F, m)	1 + 1 5,5
2 [{Pd( $\mu$ -SC <sub>6</sub> HF <sub>4</sub> -4)( $\eta$ <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )} <sub>2</sub> ]	allyl	Ha	5.59 (2H, tt)	$J_{\text{Ha}-\text{Hb}} = 6.8, J_{\text{Ha}-\text{Hc}} = 12.5$
	ý	Hb	3.82 (4H, d)	$J_{\text{Hb}-\text{Hc}} < 1$
		Hc	3.05 (4H, d)	no-ne
	SR	H4	6.82 (2H, tt)	$J_{\text{H4-F2,6}} = 8.9,$
		F2.6	$133.37^{a}$ ( <i>A</i> F m)	$J_{H4-F3,5} = 11.2$ $I_{H4-F3,5} = 21.0$
		F3 5	-135.57 (41, m) 141.42 (4E m)	$J_{\rm F2,6-F3,5} - 21.0$
<b>3</b> $[(\mathbf{P}d(\mathbf{u} \ \mathbf{SC} \ \mathbf{H} \ \mathbf{F} \ 2)(\mathbf{n}^3 \ \mathbf{C} \ \mathbf{H} \ ))]$	ollv1	1'5,5 Ha	-141.42 (41, 11) 5 52 a (2H tt)	I = -64 I = -128
$5 [(10(\mu - 5C_{6} - 141 - 2)(1 - C_{3} - 15))]_{2}]$	allyl	Hh	3.60 (4H d)	$J_{\text{Ha-Hb}} = 0.4, J_{\text{Ha-Hc}} = 12.0$
		He	2.96(4H, d)	$J_{\rm Hb-Hc}$ < 1
	SR	НЗ	7.0(2H m)	$L_{} = -81$ $L_{} = -80$
	SIC	H6	7.03(2H, m)	$J_{\text{H3}-\text{F2}} = 8.0$
		H4	7.03 (2H, m) 7.14 (2H, m)	$L_{\rm H6-H5} = 8.3$ $L_{\rm H4} = 6.4$
		H5	7.80(2H, t)	$\sigma_{\rm H4-H5} = 0.5, \sigma_{\rm H4-F2} = 0.4$
		F2	-105.84 (2F s)	
4 [{Pd( $u$ -SC <sub>2</sub> H <sub>2</sub> F-3)( $n^3$ -C <sub>2</sub> H <sub>2</sub> )} <sub>2</sub> ]	allvl	Ha	$556^{a}$ (2H, tt)	$J_{11} \dots = 72 J_{12} \dots = 124$
	unji	Hb	3.62.(4H, d)	$J_{\text{Ha}-\text{Hb}}$ $J_{\text{Ha}-\text{Hc}}$ $J_{\text{Ha}-\text{Hc}}$ $J_{\text{Ha}-\text{Hc}}$
		He	303(4H, d)	HB-HC VI
	SR	H2	7.48 (2H, d)	$J_{112} = 7.7$
		H6	7.40 (2H, dd)	$J_{H2-F3} = 8.0$
		H5	7.18 (2H, q)	$J_{115} = 5.8$
		H4	6.86 (2H, tt)	$J_{\mu_4 \ \mu_2} = 8.0, \ J_{\mu_4 \ \mu_5} = 8.0$
		F3	-117.96 (2F, s)	114-1/3
$\textbf{5} \; [\{Pd(\mu\text{-}SC_6H_4F\text{-}4)(\eta^3\text{-}C_3H_5)\}_2]$	allyl	Ha	5.52 <sup>a</sup> (2H, tt)	$J_{\text{H}_{2}\text{-H}_{2}} = 6.0, \ J_{\text{H}_{2}\text{-H}_{2}} = 12.0$
	ý	Hb	3.58 <sup>a</sup> (4H, d)	$J_{\text{Hb}-\text{Hc}} < 1$
		Hc	2.98 (4H, d)	no-ne
	SR	H2,6	7.66 (4H, q)	$J_{\rm H2.6-H3.5} = 8.8,$
			x * ▲*	$J_{\rm H2.6-F4} = 5.6$
		H3,5	6.93 (4H, t)	$J_{\rm H3.5-F4} = 8.8$
		F4	-122.25 (2F, s)	······ ·

<sup>a</sup> Broad absorption: d, doublet; m, multiplet; q, quartet; s, singlet; t, triplet.

only 0.09 ppm, the range for  $\delta$ Hb is 0.24 ppm, probably indicating a greater influence of the fluorinated substituents on these nuclei.

The <sup>1</sup>H NMR spectra of complexes 2-5 (and the <sup>19</sup>F NMR spectrum of complex 1) also show one set of resonances for the two bridging thiolate ligands.

As noted in Table 2, some <sup>1</sup>H and <sup>19</sup>F resonances are relatively broad, indicating either a dynamic process or a mixture of isomers. Mixtures of cis and trans isomers, depending on the arrangement of the allyl groups with respect to each other, have been reported for the related nickel complex  $[(\eta^3 - C_3H_5)Ni(\mu - OAr)_2Ni(\eta^3 - C_3H_5)]$  [10] and the palladium complex  $[(\eta^3-C_3H_5)Pd(\mu-SR)_2Pd(\eta^3 C_{3}H_{5}$ ] [8]. On the other hand, it has been reported that  $[(\eta^3-C_3H_5)Ni(\mu-SC_6F_5)_2Ni(\eta^3-C_3H_5)]$  is not sensitive to the relative orientation of the sulfur substituents [10].

Work aimed at investigating the dynamic behaviour of compounds 1-5 is currently under way.

### 3.1.1. X-ray crystal structure

Fig. 1 shows the diagram corresponding to the complex  $[(\eta^3 - C_3H_5)Pd(\mu - SC_6H_4F - 4)_2Pd(\eta^3 - C_3H_5)]$  (5), along with the atomic numbering scheme. Table 4 collects selected bond lengths (Å) and angles (°).

Palladium atoms have an almost square-planar co-S1–Pd1–C1A, ordination geometry: 171.0(2)°; S1-Pd2-C3A, 171.6(3)°. The Pd1S<sub>2</sub> and Pd2S<sub>2</sub> planes intersect at the sulfur bridging atoms with a dihedral angle of 49.18°.

Substituents at the sulfur atoms show a syn-exo arrangement relative to each other (see Fig. 1) with aromatic-C-S-Pd bond angles of 112.0(2) and

Table 3 NMR data of  $[Pd(SC_6F_5)(\eta^3\text{-}C_3H_5)(P(C_6H_4X\text{-}4)_3)]$  (6–9), at 298 K

Compound	Ligand			
	Nuclei		$\delta$ (ppm)	J (Hz)
$6 \left[ Pd(SC_6F_5)(\eta^3-C_3H_5)(P(C_6H_4F-4)_3) \right]$	allyl	На	5.45 (1H, tt)	$J_{\text{Ha-Hb}} = 12.8, J_{\text{Ha-Hc}} = 7.2$ $J_{\text{Ha}} = 12.8, J_{\text{Ha}} = 7.6$
		Hb	3.50 (1H, t)	$J_{\rm Hb-Hd} = 1.8, J_{\rm Hb-P} = 7.2$
		He	3.42 (1H, d)	
		Hc	3.22 (1H, t)	$J_{{ m Hc-P}} = 11.8$
		Hd	2.74 (1H, d)	
	SR	F2,6	-134.51 (2F, dd)	$J_{\text{F2,6-F3,5}} = 22.4, \ J_{\text{F2,6-F4}} = 2.3$
		F4	-162.44 (1F, t)	$J_{\rm F4-F3,5} = 20.4$
		F3,5	-164.91 (2F, m)	
	PR <sub>3</sub>	H2,6	7.46 (6H, m)	$J_{\rm H2,6-P} = 6.1, \ J_{\rm H2,6-H3,5} = 8.2$
		H3,5	7.10 (6H, t)	$J_{\rm F4-H3,5} = 8.1$
		F4	-108.80 (3F, s)	
		Р	24.18 (s)	
7 $[Pd(SC_6F_5)(\eta^3-C_3H_5)(P(C_6H_4(CF_3)-4)_3)]$	allyl	На	5.50 (1H, tt)	$J_{\text{Ha-Hb}} = 12.6, J_{\text{Ha-Hc}} = 7.0$ $J_{\text{Ha-Hd}} = 12.6, J_{\text{Ha-Hc}} = 7.7$
		Hb	3.61 (1H, t)	$J_{\rm Hb-Hd} = 1.8, \ J_{\rm Hb-P} = 7.2$
		He	3.49 (1H, d)	
		Hc	3.29 (1H, t)	$J_{\rm Hc-P} = 11.7$
		Hd	2.80 (1H, d)	
	SR	F2,6	-133.68 (2F, dd)	$J_{\text{F2,6-F3,5}} = 22.8, \ J_{\text{F2,6-F4}} = 2.6$
		F4	-163.22 (1F, t)	$J_{\rm F4-F3,5} = 20.4$
		F3,5	-164.89 (2F, m)	
	PR <sub>3</sub>	H2,6	7.68 (6H, m)	$J_{\rm H2,6-P} = 6.3,$ $J_{\rm H2.6-H3.5} = 8.5$
		H3,5	7.62 (6H, t)	
		$CF_3$	-68.82 (9F, s)	
		Р	26.68 (s)	
8 [Pd(SC <sub>6</sub> F <sub>5</sub> )( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> )(P(C <sub>6</sub> H <sub>4</sub> (OCH <sub>3</sub> )-4) <sub>3</sub> )]	allyl	На	5.50 (1H, tt)	$J_{\text{Ha-Hb}} = 12.6, J_{\text{Ha-Hc}} = 7.3$ $J_{\text{Ha-Hd}} = 12.7, J_{\text{Ha-Hc}} = 7.5$
		Hb	3.61 (1H, t)	$J_{\rm Hb-Hd} = 1.8, J_{\rm Hb-P} = 7.3$
		He	3.49 (1H, d)	
		Hc	3.29 (1H, t)	$J_{\rm Hc-P} = 11.9$
		Hd	2.80(1H, d)	
	SR	F2,6	-133.68 (2F, dd)	$J_{\rm F2,6-F3,5} = 22.4,$
				$J_{\rm F2,6-F4} = 2.3$
		F4	-163.22 (1F, t)	$J_{\rm F4-F3,5} = 20.6$
		F3,5	-164.89 (2F, m)	
	PR <sub>3</sub>	H2,6	7.68 (6H, m)	$J_{\text{H2,6-P}} = 6.3, \ J_{\text{H2,6-H3,5}} = 8.5$
		H3,5	7.62 (6H, t)	
		$CH_3$	-68.82 (9F, s)	
		Р	26.68 (s)	
9 [Pd(SC <sub>6</sub> F <sub>5</sub> )( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> )(P(C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> )-4) <sub>3</sub> )]	allyl	На	5.44 (1H, tt)	$J_{\text{Ha-Hb}} = 12.8, J_{\text{Ha-Hc}} = 7.2$ $J_{\text{Ha-Hd}} = 12.8, J_{\text{Ha-Hc}} = 7.5$
		Hb	3.51 (1H, t)	$J_{\rm Hb-Hc} {=} 1.8, \; J_{\rm Hb-P} {=} 7.2$
		He	3.39 (1H, d)	
		Hc	3.19 (1H, t)	$J_{\rm Hc-P} = 11.9$
		Hd	2.68 (1H, d)	
	SR	F2,6	-133.50 (2F, dd)	$J_{\text{F2,6-F3,5}} = 22.6, J_{\text{F2,6-F4}} = 2.5$
		F4	-164.77 (1F, t)	$J_{\rm F4-F3,5} = 20.6$
		F3,5	-164.91 (2F, m)	
	PR <sub>3</sub>	H2,6	7.35 (6H, m)	$J_{\rm H2,6-P} = 6.2, J_{\rm H2,6-H3,5} = 8.6$
		H3,5	7.15 (6H, t)	
		$CH_3$	2.34 (9H, s)	
		Р	24.29 (s)	

Broad absorption: d, doublet; m, multiplet; q, quartet; s, singlet; t, triplet.



Scheme 1.

111.1(2)°, both of which are within the expected range for a pyramidal environment around the sulfur atoms. Similar structural features have recently been reported for the complex [(dppe)Pd( $\mu$ -SC<sub>6</sub>H<sub>4</sub>Me-4)<sub>2</sub>Pd( $\eta$ <sup>3</sup>-C<sub>3</sub>-H<sub>5</sub>)]ClO<sub>4</sub> [11]. The allyl and the PdS<sub>2</sub> planes in **5** form angles of 5.17 and 20.18°.

Complex 5 shows a *cis* arrangement with both unsaturated moieties pointing in the same direction.

Allyl angles are 154.2(15) and 149.6(24)°. The C–C–C angles in the allyl groups are within the range 141.46–154.2°.

### 3.2. Monometallic complexes

Reaction of the fluorothiolate dinuclear complex  $[(\eta^3-C_3H_5)Pd(\mu-SC_6F_5)_2Pd(\eta^3-C_3H_5)]$  (1) with  $P(C_6H_4-X-4)_3$  (X = F, CF<sub>3</sub>, OCH<sub>3</sub> and CH<sub>3</sub>) (1:1 molar ratio) in acetone yields the corresponding mononuclear perfluorobenzenethiolato compounds:  $[Pd(SC_6F_5)(\eta^3-C_3H_5)(P(C_6H_4X-4)_3)]$  (X = F, 6; CF<sub>3</sub>, 7; OCH<sub>3</sub>, 8 and CH<sub>3</sub>, 9), as shown in Reaction (2). The related compounds  $[Pd(OC_6H_4CN-4)(\eta^3-C_3H_5)(PCy_3)]$  [20] and  $[Pd(OAr)(\eta^3-C_4H_7)(PPh_3)]$  [21] are also known.

 $[(\eta^{3}-C_{3}H_{5})Pd(\mu-SR)_{2}Pd(\eta^{3}-C_{3}H_{5})] + 2P(C_{6}H_{4}X-4)_{3} - - - 2[Pd(SR)(\eta^{3}-C_{3}H_{5})(P(C_{6}H_{4}X-4)_{3})]$ 

$$\begin{array}{c|c} \mathbf{X} \\ \mathbf{\underline{6}} & \mathsf{F} \\ \mathbf{7} & \mathsf{CF}_3 \\ \mathbf{\underline{8}} & \mathsf{OCH}_3 \\ \mathbf{9} & \mathsf{CH}_3 \end{array} \tag{2}$$

Compounds 6-9 are yellow, diamagnetic, crystalline solids, which are soluble in acetone and dichloromethane. These complexes are relatively stable in the solid state and in solution for several months.

The <sup>1</sup>H NMR spectra of complexes 6-9 (Table 3)

Table 4

Selected bond distances (Å) and angles (°) of  $[\{Pd(\mu\text{-}SC_6H_4F\text{-}4)(\eta^3\text{-}allyl)\}_2]$  (5)

Bond lengths			
Pd1-S1	2.3693(12)	Pd2-S1	2.3677(12)
Pd1-C1	2.150(3)	Pd2-C3	2.131(4)
Pd1-C2A	2.099(11)	Pd2-C4A	2.052(3)
Pd1-C2B	2.121(16)	Pd2–C4B	2.174(19)
S1-C5	1.781(4)	C5-C6	1.376(6)
C5-C10	1.385(6)	F1-C8	1.365(6)
Bond angles			
S1-Pd1-S1a	83.25(4)	S1-Pd2-S1a	83.31(4)
S1-Pd1-C1	104.87(11)	S1-Pd1-C1a	171.35(11)
S1-Pd2-C3	104.54(11)	S1-Pd2-C4A	136.79(12)
S1-Pd2-C4B	137.53(9)	Pd1-S1-C5	112.10(14)
Pd2-S1-C5	111.33(15)	Pd1-S1-Pd2	85.71(4)
C2A-Pd1-C2B	27.5(8)	C4A-Pd2-C4B	21.9(5)

indicate that the  $\eta^3$ -ligand is rigid at room temperature—the spectra show a unique set of five resonances of equal intensity for the allylic protons Ha to He (Scheme 1). The shielding order for the allylic protons is Hd > Hb > He > Hc > Ha, with a spin–spin coupling pattern that is the same as that observed for the chloride complex [PdCl( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)] [22], where the nuclei *trans* to phosphine (Hb and Hc) are coupled to <sup>31</sup>P. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of complexes **6–9** show a single resonance.

Both the proton chemical shifts of allylic nuclei and  ${}^{1}H^{-31}P$  spin-spin coupling constants do not seem to be sensitive to the nature of the *para*-substituent on the phosphine ligand.

Although the fragment  $[PdX(\eta^3-allyl)]$  has been shown to promote the addition of the X ligand to the allylic skeleton when X = OPh [21] and SR [9], no such reaction was observed under the conditions used in this work.

#### 4. Supplementary material

Crystallographic data (excluding structure factors) for the reported structure have been deposited with the



Fig. 1. Structure of  $[(\eta^3-C_3H_5)Pd(\mu-SC_6H_4F-4)_2Pd(\eta^3-C_3H_5)]$  (5) with thermal ellipsoids at 30% probability level. H atoms are omitted for clarity.

Cambridge Crystallographic Data Centre, CCDC No. 144419 for compound **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk).

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