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# Synthesis and crystal structures of new palladium catalysts for the hydromethoxycarbonylation of alkenes

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# 1. Introduction

Triphenylphosphine as a ligand and complexes of palladium and triphenylphosphine have featured prominently in coordination chemistry [1] and in their applications in organic chemistry and catalysis [2,3]. One important and well documented reaction in which palladium phosphine complexes are employed is the alkene carbonylation reations in which their role hinges on two important types of complexes; low-coordinate and hemilabile species [4]. In addition Buchwald has also shown how good tertiary phosphines are as supporting ligands for most palladium-catalyzed coupling reactions [5].

Dinuclear Pd(I)–Pd(I) complexes have been shown as precursors in useful catalytic processes [6]. The tuning of the electronic and steric properties around the metal–metal bonds of these complexes makes them quite interesting and using ligands like phosphine in this regard helps since they can also be easily monitored by a number of spectroscopic methods. The phenyl rings in these Pd(I)–Pd(I) dimers have been shown to adopt an unusual  $\eta^2:\eta^2$  bridging mode and high stability on exposure to air [6]. Some structural examples from literature of such complexes include; Pd<sub>2</sub>Br<sub>2</sub>( $\mu$ -P<sup>t</sup>Bu<sub>2</sub>Ph<sub>2</sub> [6], [Pd<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN)<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub> [7], [Pd<sub>2</sub>{(PPh<sub>2</sub>)C<sub>20</sub>H<sub>12</sub>-OMe}<sub>2</sub>](BF<sub>4</sub>) [8] and [Pd<sub>2</sub>{PCy<sub>2</sub>(PhAr)}<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> [9]. Different synthetic routes were used in the preparation of these compounds. These included the reaction of cationic and neutral palladium complexes [6], the use of cationic species where two

# ABSTRACT

The preparation and structural characterization of dimeric Pd(I)–Pd(I) complex [Pd<sub>2</sub>{(PPh<sub>3</sub>)(O-SO<sub>2</sub>CF<sub>3</sub>)}<sub>2</sub>].CH<sub>2</sub>Cl<sub>2</sub> (**1**) and three palladium center [Pd<sub>3</sub>{(PPh<sub>3</sub>)(OSO<sub>2</sub>CF<sub>3</sub>)}<sub>2</sub>] (**2**) and [Pd<sub>3</sub>(PPh<sub>3</sub>)<sub>4</sub>](SO3CF<sub>3</sub>)<sub>2</sub> (**3**) complexes are reported. The complexes exhibit coordination in which the phosphine phenyl ring is used to stabilize Pd(I) centers in (**1**) and, Pd(I) and Pd(0) centers in (**2**) and (**3**) by acting as  $\pi$  electron donors. The complexes were characterized by single crystal X-ray crystallography.

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ligands [7] or four ligands [8] were displaced resulting in Pd-arene interactions.

A few three-metal-center palladium complexes have also been reported and perhaps the closest to the three-center-metal structures reported here is  $[Pd_3(PPh_3)_4](BF_4)_2$  [10]. In fact only one structure in which a three-metal-center is bridged by a P atom and the phenyl rings of the phosphine ligand are known [10]. They synthesized there complex via the reduction of a dimeric Pd(II) species in the presence of an alcohol (MeOH, <sup>*i*</sup>PrOH or <sup>*t*</sup>BuOH). However there are examples of related three-metal-center palladium complexes such as  $[(CH_3NC)_8Pd_3]^{2+}(PF_6)_2^-$  and  $[(CH_3NC)_6\{Ph_3P\}_2Pd_3](PF_6)_2$  [11]. Wasserman et al. [11], employed a method where complexes with  $d^8$  and  $d^{10}$  electronic configurations were reacted resulting in tripalladium complexes. Several examples of similar but bridged complexes of phosphorus (mainly biphosphines) are also known and can be found in literature [11 and references therein].

Herein, we report the synthesis and characterization of the dimeric Pd(I)–Pd(I) complex  $[Pd_2{(PPh_3)(OSO_2CF_3)}_2]$ .CH<sub>2</sub>Cl<sub>2</sub> (1) and three palladium center  $[Pd_3{(PPh_3)(OSO_2CF_3)}_2]$  (2) and  $[Pd_3(PPh_3)_4](SO_3CF_3)_2$  (3).

## 2. Material and methods

# 2.1. Synthesis

# 2.1.1. Preparation of **1** and **2**

A solution of PPh<sub>3</sub> (525 mg, 2 mmol) in dichloromethane (DCM) (5 mL) was added to a stirred solution of  $Pd(OAc)_2$  (224.5 mg,



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1 mmol) in DCM (5 mL). Removal of the solvent *in vacuo* left a yellow crystalline solid. The solid was dissolved in 5 mL of DCM under argon. After cooling to 0 °C, a solution of CF<sub>3</sub>SO<sub>3</sub>H (450 mg, 266  $\mu$ L, 3 mmol) in 1 mL of DCM was added drop-wise over a period of 5 min. The resulting dark brown mixture was allowed to warm to room temperature and in an atmosphere of argon, exposed to vapors of diethyl ether for 18 h resulting in the slow deposition of red crystals of **1** (162 mg), m.p. 125 °C (decomp). The supernatant was removed from the crystals and further exposed to vapors of diethyl ether at -5 °C for 12 h. This resulted in the deposition of brown plates of **2** (85 mg), m.p. 145 °C (decomp).

## 2.1.2. Preparation of 3

Reaction of PPh<sub>3</sub> (525 mg, 2 mmol) and Pd(OAc)<sub>2</sub> (224.5 mg, 1 mmol) in 10 mL DCM followed by evaporation of solvent furnished a yellow crystalline solid which was taken up in methanol (7 mL). The stirred dark yellow solution was cooled to 0 °C in an atmosphere of argon, and CF<sub>3</sub>COOH (450 mg, 266  $\mu$ L, 3 mmol) was added slowly from a micro syringe. The solution which first became bright red and later changed to a dark reddish-brown solution was exposed to vapors of diethyl ether under argon at 0 °C for 12 h. This resulted in the deposition of reddish-brown crystals of **3** (144 mg), m.p. 167 °C (decomp). Additional crystals of **3** (45 mg) were obtained on leaving the supernatant solution at -10 °C for 12 h.

# 2.1.3. Crystallography

Crystals of **1**, **2** and **3** were grown by diffusion of vapors of diethyl ether into solutions of the complexes in dichloromethane or methanol at room temperature. Single crystals X-ray diffraction data were collected on a Bruker X8 Apex II 4K Kappa CCD diffractometer using Mo K $\alpha$  (0.71073 Å) radiation with  $\varphi$  and  $\omega$ -scans at 100(2) K. The initial unit cell and data collection were achieved by

#### Table 1

Crystal data and structural refinement for 1, 2 and 3.

the Apex 2 [12] software utilizing COSMO [12] and were corrected for Lorentz, polarization and absorption effects using SADABS [12]. The structures were solved by Patterson method using SHELXS97 [13] and refined through full-matrix least-squares cycles using the SHELX97 [13] software package with  $\Sigma(/Fo/-/Fc/)^2$  being minimized. All non-H atoms were refined with anisotropic displacement parameters.

Aromatic H atoms were placed in geometrically idealized positions (C–H = 0.95 Å) and constrained to ride on their parent atoms, with  $U_{iso}(H) = 1.2U_{eq}(C)$ . The deepest residual electron-density holes (-0.72, -0.66 and -1.71 e.Å<sup>-3</sup> for **1**, **2** and **3** respectively) are located 0.78 Å from Pd2 in **1**, 0.94 Å from Pd2 in **2** and 0.35 Å from Pd1 in **3**. The highest peaks (0.69, 0.54 and 1.37 e.Å<sup>-3</sup> for **1**, **2** and **3** respectively) are located 1.07 from Pd2 in **1**, 0.86 Å from F1 in **2** and 0.72 Å from Pd2 **3**. Crystal data and details for data collection and refinement are given in Table 1.

All structures were checked for solvent accessible cavities using PLATON [14] and the graphics performed with DIAMOND [15].

#### 2.1.4. NMR spectroscopy

<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR data was collected using 300 MHz Varian INOVA spectrometer with 5 mm 4 nucleus probe. Palladium complexes **1**, **2** and **3** are sparingly soluble in most solvents (including ether, acetone and the alcohols), while in solutions of e.g.  $CH_2Cl_2$  and DMSO, rapid deposition of palladium is observed. Due to their marked instability in solution it was possible to obtain meaningful NMR spectra NMR spectra only of compound **3** and this required the use of several fresh samples with  $CD_2Cl_2$  as solvent. The <sup>1</sup>H, <sup>13</sup>C{H} and <sup>31</sup>P{H} spectra were analyzed in conjunction with 1D-TOESY, HSQC and HMBC correlation spectra. It is noted here that the NMR data for compound **3** were found to agree with those of  $[Pd_3(PPh_3)_4](BF_4)_2$  [10].

	1	2	3
Empirical formula	C <sub>39</sub> H <sub>32</sub> Cl <sub>2</sub> F <sub>6</sub> O <sub>6</sub> P <sub>2</sub> Pd <sub>2</sub> S <sub>2</sub>	C <sub>38</sub> H <sub>30</sub> F <sub>6</sub> O <sub>6</sub> P <sub>2</sub> Pd <sub>3</sub> S <sub>2</sub>	C <sub>74</sub> H <sub>60</sub> F <sub>6</sub> O <sub>6</sub> P <sub>4</sub> Pd <sub>3</sub> S <sub>2</sub>
Formula weight	1120.41	1141.88	1666.44
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P2(1)/c	$P\overline{1}$	P1
Unit cell dimensions			
a (Å)	13.6664(9)	8.6528(5)	9.451(5)
b (Å)	13.7718(9)	9.0808(5)	12.709(5)
c (Å)	23.9657(14)	13.5872(8)	14.627(5)
α (°)	90	84.0030(10)	80.583(5)
$\beta$ (°)	111.839(3)	77.3870(10)	81.045(5)
γ (°)	90	70.1960(10)	72.712(5)
Volume (Å <sup>3</sup> )	4186.9(5)	979.68(10)	1644.2(12)
Ζ	4	1	1
$D_{\text{calc}}$ (Mg/m <sup>3</sup> )	1.777	1.935	1.683
Absorption coefficient (mm <sup>-1</sup> )	1.236	1.625	1.045
F(000)	2224	560	836
Crystal size (mm <sup>3</sup> )	$0.19\times0.04\times0.04$	$0.31 \times 0.14 \times 0.02$	$0.17 \times 0.16 \times 0.05$
$\theta$ range for data collection (°)	1.61-28.39	2.39-28.46	1.69-28.08
Index ranges	-18/18, -18/18, -32/32	-11/11, -12/12, -18/18	-12/12, -16/16, -19/19
Reflections collected	57832	23766	61316
Independent reflections [R <sub>int</sub> ]	10469 [0.0644]	4922 [0.0295]	7965 [0.0355]
Completeness to $\theta = 28.35^{\circ}$	99.7%	99.2%	99.2%
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
Maximum and minimum transmission	0.9522 and 0.7991	0.9682 and 0.6327	0.9496 and 0.8424
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	10469/38/532	4922/28/259	7965/0/430
Goodness-of-fit on F <sup>2</sup>	1.026	1.034	1.102
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0318$ , $wR_2 = 0.0597$	$R_1 = 0.0190, wR_2 = 0.0485$	$R_1 = 0.0357, wR_2 = 0.0971$
R indices (all data)	$R_1 = 0.0535$ , $wR_2 = 0.0664$	$R_1 = 0.0210$ , $wR_2 = 0.0500$	$R_1 = 0.0483, wR_2 = 0.1135$
Largest difference peak and hole $(e.Å^{-3})$	0.690 and -0.717	0.530 and -0.664	1.374 and -1.708

# 3. Results and discussion

Exposure of a solution of (PPh<sub>3</sub>)<sub>2</sub>Pd(OCOCH<sub>3</sub>)<sub>2</sub> and 3 mol equivalents of CF<sub>3</sub>SO<sub>3</sub>H in methanol or dichloromethane under argon to the vapors of diethyl ether for 24 h furnished crystals of two palladium complexes of compound (1) [(PPh<sub>3</sub>)<sub>2</sub>Pd<sub>2</sub>(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] (red prisms) and compound (2) [(PPh<sub>3</sub>)<sub>2</sub>Pd<sub>3</sub>(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] (brown plates) in the ratio of *ca* 2:1 and combined vield (based on Pd) of *ca* 55%. Compound (3) [(PPh<sub>3</sub>)<sub>4</sub>Pd<sub>3</sub>].(SO<sub>3</sub>CF<sub>3</sub>)<sub>2</sub> was obtained as reddish-brown prisms (60% yield) directly by treating the 1 Pd(OAc)<sub>2</sub>: 2 PPh<sub>3</sub> complex 2 in MeOH with three equivalents of CF<sub>3</sub>SO<sub>3</sub>H. It appears that the formation of the complexes involves reduction of the palladium(II) starting material possibly with methanol and small quantities of water in the case of compound **3** [10,16,17] and with adventitious water and triphenylphosphine as the reducing agent in the case of compounds 1 and 2 [10]. The mechanism of the reactions that lead to compounds 1 and 2 is the subject of further investigation.

Compounds **1**, **2** and **3** are remarkably stable in solid state and remained unchanged on exposure to air for three months. This is unexpected for compounds containing palladium in the +1 (compound **1**) and 0 and +1 oxidation states (compound **2** and **3**).

Compounds 1, 2 and 3 showed catalytic activity in the hydromethoxycarbonylation of alkenes [18]. On reacting the palladium complex  $[(PPh_3)_4Pd(OSO_2CF_3)_2]$  or  $[(PPh_3)_2PdCl_2]$  in the system normally employed [ $L_2PdX_2$ : L: HX = 1: 6: 6–20; where L = PPh<sub>3</sub> and HX = HCl or HOTf; Alkene: MeOH (3:1–1:1), 30-60 Bar CO] [18], the hydromethoxycarbonylation normally starts at around 90 °C when the temperature of the reaction is ramped from room temperature to 100 °C at a rate of 4.5 °C per minute. The rate of the reaction is indicated by the onset in a reduction of reactor pressure. When the reaction temperature reaches 100 °C there is a period of 5–10 min before steady state uptake of  $CO_2$  is attained. When the above catalysts are replaced by complexes 1, 2 and 3, the reaction starts at 80 °C and when the temperature reaches 100 °C the steady state condition is already attained. This difference is tentatively ascribed to the direct conversion of the complex to the active palladium hydride complex in the reaction medium without the reduction normally required (Eqs. (1) and (2)).



**Fig. 1.** View of **1** with thermal ellipsoids shown at 50% probability level. Hydrogen atoms have been omitted for clarity.

$$L_2Pd_3(OTf)_2 + 2HOTf + 2L \rightarrow 2L_2PdH(OTf) + L_2Pd(OTf)_2$$
(1)

$$\begin{array}{c} L_2PdH(OTf)+CH_2=CH_2+CO\rightarrow L_2PdH(COCH_2CH_3)+CH_3OH\\ L_2PdH(OTf)+CH_3CH_2COOCH_3 \end{array} \tag{2}$$

However, there is a little difference in the Turnover Frequency (TOF) of all of the above catalysts when the steady-state condition at 100 °C is attained. It is of interest to note that related palladium(I) complexes showed catalytic activity in e.g. the amination of aryl halides [19].



Fig. 2. View of 2 with thermal ellipsoids shown at 50% probability level. Hydrogen atoms have been omitted for clarity.



Fig. 3. View of 3 with thermal ellipsoids shown at 50% probability level. Hydrogen atoms have been omitted for clarity.

## 3.1. Molecular and crystal analysis

Single crystal X-ray diffraction was used to determine the absolute structures of complexes **1** to **3**. ORTEP diagrams for the three structures of  $[(PPh_3)_2Pd_2(OSO_2CF_3)_2]$  (**1**),  $[(PPh_3)_2Pd_3(O-SO_2CF_3)_2]$  (**2**) and  $[(PPh_3)_4Pd_3](SO_3CF_3)_2$  (**3**) are given in Figs. 1–3 respectively. Selected bond distances and angles are presented in Tables 2, 3 and 4. In all three complexes the main feature is a stabilization of Pd(0) and/or Pd(I) center by the phosphine phenyl rings.

Complex **1** crystallizes with two molecules in asymmetric unit, the complex and a dichloromethane solvent molecule. In the structure of **1** the phosphine ligands are arranged in a head-to-tail fashion and coordinated with two palladium atoms through the phosphorus atoms and a phenyl ring from each of the phosphines, and in addition to the oxygen atoms of the two triflate anions (Fig. 1). The coordination of the palladium atoms to the phenyl ring could be described as  $\eta^2$  even though the Pd–C<sub>ortho</sub> bond distances seem slightly longer 2.542(3) and 2.506(3) Å. The Pd–C<sub>ipso</sub> bond distances are 2.325(2) and 2.381(3) Å and are all close to the sum of

Selected bond distances an	1 angles (	A, °) for	complex 1	۱.
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Distances			
Pd1–Pd2	2.5432(3)	Pd1-C18 <sub>ortho</sub>	2.542(3)
Pd1–P2	2.2194(7)	Pd2-C32 <sub>ortho</sub>	2.506(3)
Pd2–P1	2.2210(7)	Pd1-O1	2.2062(19)
Pd1-C13 <sub>ipso</sub>	2.325(2)	Pd2-O4	2.1785(19)
Pd2-C31 <sub>ipso</sub>	2.381(3)	Pd2–P1	2.2210(7)
Pd1–P2	2.2194(7)	C31-C32	1.413(4)
C31-C36	1.409(4)	C13-C14	1.405(4)
C13–C18	1.406(4)		
Angles			
O1-Pd1-Pd2	104.22(5)	O4-Pd2-Pd1	104.30(5)
01-Pd1-C13	97.61(8)	O4-Pd2C31	97.95(8)
P1-Pd2-Pd1	71.78(2)	P2-Pd1-Pd2	72.20(2)
C18-Pd1-Pd2	90.95(7)	C31–Pd2–Pd1	85.64(7)
C14-C13-C18	119.2(2)	C32-C31-C36	118.8(2)

van der Waals radii of Pd and carbon atoms. There is a significant tilt of the arene rings which is comparable to that of calculated structure in which the uncoordinated phenyl rings are replaced with Me groups and the experimentally determined structure  $Pd_2Br_2(\mu-P^tBu_2Ph)_2$  [6]. Besides the  $C_{ipso}-C_{ortho}$  distances of the arene rings are only slightly affected with the distances ranging between 1.405(4) and 1.413(4) Å indicating a fair amount of  $\pi$  electron delocalization on the ring and therefore stabilization of the system by the arene  $\pi$ -electron density and the palladium atoms. These  $Pd-C_{ortho}$  and  $Pd-C_{ipso}$  bond distances are however notably

Table 3

Selected inter-atomic bond distances (Å) and angles (°) for complexes **2**, **3** and for  $[Pd_3(PPh_3)_4](BF_4)_2$ .

	2	3	Kanna et al. [10]
Distances			
Pd1–Pd2	2.57984(16)	2.6622(7)	2.6587(3)
$Pd-PPh_3$ [Pd-O in 2]	[2.2228(13)]	2.3548(11)	2.345(1)
$Pd-PC_6H_5Ph_2$	2.2338(4)	2.2453(12)	2.255(1)
Pd-C <sub>ipso</sub>	2.1962(15)	2.176(3)	2.183(4)
Pd-C <sub>ortho</sub>	2.2937(16)	2.283(3)	2.317(4)
Pd-C <sub>meta</sub>	2.3514(17)	2.394(3)	2.397(5)
Pd-C <sub>para</sub>	2.2665(17)	2.266(3)	2.288(4)
C <sub>ipso</sub> -C <sub>para</sub>	1.398(3)	1.428(5)	1.434(7)
C <sub>ipso</sub> -C <sub>para</sub>	1.419(2)	1.428(5)	1.437(6)
Angles			
$PPh_3 - Pd - PC_6H_5Ph_2$	[100.65(4)]	102.47(3)	101.35(4)
[P–Pd–O] in <b>2</b>			
Pd-Pd-C <sub>para</sub>	92.68(5)	92.26(9)	_
PPh <sub>3</sub> -Pd-C <sub>para</sub>	92.80(6)	95.16(9)	_
$O-Pd-C_{para}$ in <b>2</b>			
$PC_6H_5Ph_2-Pd-Pd$	73.834(12)	70.11(3)	71.08(3)
C <sub>ipso</sub> -Pd1-Pd2	93.93(4)	92.55(9)	
Cipso-Pd1-Pd2	86.07(4)	87.45(9)	
PPh <sub>3</sub> -Pd-Pd [O-Pd-Pd]	[174.03(3)]	172.57(2)	172.27(3)
Pd-Pd-Pd	180	180	180
Rms dev. Pd-PPC	0.0540	0.1083	0.0932
Pd–POC in 2			
Reference	This work	This work	Kannan
			et al., 1998 [10]

**Table 4**C-H...O hydrogen bond geometry of compounds 1, 2 and 3.

	D-HA	D-H/Å	HA/Å	DA/Å	$< D-HA/^{\circ}$	Symmetry operator
1	C16-H1602	0.95	2.34		148	$-x, \frac{1}{2} + y, \frac{1}{2} - z$
	C32-H3205	0.95	2.51	3.211(4)	131	$1 - x$ , $\frac{1}{2} + y$ , $\frac{1}{2} - z$
	C39-H3906	0.95	2.57	3.310(5)	131	$1 - x$ , $\frac{1}{2} + y$ , $\frac{1}{2} - z$
2	C4-H4O3	0.95	2.45	3.233(2)	139	-1 + x, y, z
	C8-H801	0.95	2.56	3.478(2)	162	-1 + x, $1 + y$ , z
	C18-H18O2	0.95	2.54	3.271(3)	134	−x, −y, 1 − z
3	C18-H18O3	0.95	2.45	3.272(6)	150	-1 + x, $1 + y$ , z
	C27-H2701	0.95	2.59	3.378(6)	141	-1 + x, y, z

Table 5

C–H... $\pi$  Intermolecular interactions for compounds 1, 2 and 3.

	С-Нπ	Hπ/Å	$<$ C $-$ H $\pi/^{\circ}$	Cπ/Å	Symmetry operator
1	C3-H3Cg2	2.99	136	3.732(3)	$1 - x$ , $\frac{1}{2} + y$ , $\frac{1}{2} - z$
2	C10-H10Cg2	2.69	152	3.553(2)	−x, 1−y, −z
	C15-H15Cg2	2.63	152	3.498(2)	1 + x, y, z
3	C4–H4Cg7	2.99	137	3.748(5)	1 + x, y, z

longer than the Pd–P bond distances 2.2210(7) and 2.2194(7) Å and are in good agreement with Pd–P separations in similar dicationic species [20]. The Pd–O distances are 2.1785(19) and 2.2062(19) Å. The Pd–Pd separation distance is 2.5432(3) Å which lies within the range of Pd–Pd dimers, Pd–Pd<sub>min</sub> 2.4878(7) and Pd–Pd<sub>max</sub> 3.1882(6) Å [7].

There is only one structure from literature,  $[Pd_3(PPh_3)_4](BF_4)_2$ , that is similar to compounds 2 and 3 [10]. In fact the reported structure is very similar to compound 3 with the only difference being the counterions used. The centrosymetric Pd<sub>3</sub> cation structures of complexes **2** and **3** are given in Figs. 2 and 3. Each of the structures consists of a linear chain described by O-Pd-Pd-Pd-O in **2** and P-Pd-Pd-Pd-P in **3** and coordinated to  $Ph_2P-C_6H_6$ groups, in a head-to-tail fashion. In compound 2 the coordination of Pd1 is to an O atom from the triflate anion, to a P atom of the triphenylphosphine ligand with Pd2 being stabilized by an arene ring of the triphenylphosphine whereas in compound 3 the coordination of Pd1 is to two triphenylphosphine ligands with the stabilization of Pd2 done by an arene ring of one of the triphenylphosphine ligands, and with the counterion (the triflate) kicked out of the coordination sphere. There might also be some interaction between the P atoms holding the arene rings and the central Pd atom [P1-Pd = 2.9045(4) and 2.8391(12) Å in 2 and 3respectively]. The bridging of the two Pd atoms in the chain was described as  $\mu$ - $\eta$ :<sup>2</sup> $\eta$ <sup>2</sup>-diene (Figs. 1 and 2) with the oxidation states of the palladium atoms as Pd(I)–Pd(0)–Pd(I) [10]. The arene rings bond to the palladium atoms through four carbon atoms, where the Pd–C<sub>ipso</sub> and Pd–C<sub>para</sub> bond distances are shorter [2.1962(15) and 2.2665(17) in compound **2**, and 2.176(3) and 2.266(3) Å in compound **3**] while the Pd–C<sub>ortho</sub> and Pd–C<sub>meta</sub> are longer comparatively [2.2937(16) and 2.3514(17) in compound **2**, and 2.283(3) and 2.394(3) Å in compound **3**]. These distances compare well with those of [Pd<sub>3</sub>(PPh<sub>3</sub>)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (Table 3) [10].

The Pd1–Pd2 bond distance in compound **2** (2.57984(16) Å) is shorter than those in compound **3** (2.6622(7) Å) and  $[Pd_3(PPh_3)_4](BF_4)_2$  (2.6587(3) Å). In compound **2** coordination is to an oxygen atom whereas in **3** and  $[Pd_3(PPh_3)_4](BF_4)_2$  coordination is to phosphorus atoms. The distances are however still within the range of Pd–Pd dimers, Pd–Pd<sub>min</sub> 2.4878(7) and Pd–Pd<sub>max</sub> 3.1882(6) Å [7]. The Pd–O bond distance in **2** (2.2228(13)) is slightly longer that those in compound **1** [2.2062(19) and 2.1785(19) Å]. In compound **3**, the Pd–P bond distances of the phosphine with the coordinating arene ring and the second phosphine are different. Pd–PPh<sub>3</sub> is longer (2.3548(11) Å) than Pd–PC<sub>6</sub>H<sub>5</sub>Ph<sub>2</sub> (2.2453(12) Å). The respective distances in and  $[Pd_3(PPh_3)_4](BF_4)_2$  are 2.345(1) and 2.255(1) Å [10].

In all three complexes, the geometry around each palladium atom is square planar with a slight deviation from ideal orthogonality. The angles around the palladium atoms range between 70.11(3) in complex **3** to  $104.22(5)^{\circ}$  in complex **1** (Tables 2 and 3). P1–Pd2–O4 and P2–Pd1–O1 are the wider angles in **1**. P1–Pd2–O3 and P1–Pd2–P2 are the widest in **2** and **3** respectively. This is as a result of the arene rings bonding to palladium atoms. Besides the least-squares plane of atoms coordinated to the palladium centers showed only a small deviation in each complex (Tables 2 and 3).

In the crystals of the three compounds, molecules are connected through weak C-H...O hydrogen bond interactions (Table 4). These interactions involve aromatic ring hydrogen's and oxygen atoms of the coordinating triflate anion. In compound 1 these interactions are between molecules that are related by a screw-axis along the crystallographic *a*-axis. In the crystal structures of **2** and **3** hydrogen bonded molecules are related by translation along the crystallographic *a* and *b* axes. In addition to the weak C–H…O hydrogen bonds', packing in the three compounds is also aided by C–H... $\pi$ intermolecular interactions (Table 5). Packing is further stabilized by heteroatom... $\pi$  intermolecular interactions in the compounds **2** and **3** (and not in **1**). In **2** there are two S–0... $\pi$  intermolecular interactions [O1...Cg4 and O1...Cg5 = 3.512(2) Å; S1-O1...Cg4 and S1-O1...Cg5 =  $144.7(9)^{\circ}$ ; symmetry operators, 1 - x, -y, 1 - z and 1 + x, -1 + y, z respectively]. In compound **3**, there C–F... $\pi$ intermolecular interactions that connect molecules along the



Fig. 4. <sup>31</sup>P NMR spectrum of complex 3.

crystallographic *b* axis [F1...Cg5 = 3.989(4) Å, C37-F1...Cg5 =  $160.6(3)^{\circ}$  and F3...Cg = 3.601(4) Å, C37-F3...Cg7 =  $127(2)^{\circ}$ .

#### 4. NMR spectroscopy analysis

Solutions of compound **3** in  $CD_2Cl_2$  showed rapid depositions of palladium and as such several fresh samples of the solution had to be used to obtain any meaningful data. The <sup>31</sup>P NMR spectrum of compound **3** showed the resonances of P atoms in two different environments as in the case of the solid state. The two resonances occur at 42.65 and 9.18 ppm. The spectrum is completely symmetrical around the midpoint consistent with an *AA'BB'* type system in which each phosphorus gives rise to a symmetrical 10-line pattern (see Fig. 4 and inset). This is agreement with what was observed for the compound  $[Pd_3(PPh_3)_4](BF_4)_2$  [10]. The singlets at 37.72 and 23.29 ppm, arise from decomposition almost immediately after dissolution and continues to grow rapidly.

As in the case of related palladium complexes [20] where an arene ring is coordinated to a Pd, the <sup>1</sup>H and <sup>13</sup>C signals are shifted to higher field compared to corresponding non-coordinated arenes. The coordinated phenyl ring of **3** shows three <sup>1</sup>H resonances at 7.05 (multiplet), 6.04 (broad triplet,  $J \approx 7.4$  Hz) and 4.87 (broad triplet,  $J \approx 7.42$  Hz) in the ratio 1:2:2. The corresponding <sup>13</sup>C resonances appear at 88.09, 117.05 and 107.36 ppm respectively. The remaining proton signals appear in the region 7.20–7.55 ppm. The aromatic CH carbons resonante at 135.72, 133.75, 131.62, 131.49, 129.65 and 129.60 ppm, while their *ipso*-carbons, resonate at 132.87, 128.90 and 125.08 ppm.

The NMR data is essentially consistent with the structure and symmetry of compound **3** in the solid state. However, the solid-state structure shows that the coordination of each of the two phenyl rings can be described as through a  $\eta^2$ -mode to the central Pd and to the terminal Pd atoms. The modes of coordination are not unprecedented [20].

## 5. Conclusions

In summary we have presented the synthesis structures of three palladium complexes as characterized by single crystal X-ray crystallography and for compound **3**, NMR spectroscopy. The structures have provided us with an insight as to why they are active as catalysts for hydromethoxycarbonylation of alkenes. The three complexes reported here use a phosphine phenyl ring to stabilize the Pd(I) centers in complex (1) and Pd(I) and Pd(0) centers in complexes (2) and (3).

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# Appendix A. Supplementary material

CCDC 803811; 803812; 803813 contains 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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