

Pd(O₂CCF₂CF₃-O)₂(dppf) and PdAg(μ-O₂CCF₂CF₃)₂(O₂CCF₂CF₃-O)-(dppf) [dppf = 1,1'-bis(diphenylphosphino)ferrocene]: A stable Pd(II) phosphine carboxylate as a precursor to heterobimetallic carboxylates

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Single crystal X-ray diffraction analysis of Pd(O₂CCF₂CF₃-O)₂(dppf) **1** shows that one of the two unidentate fluoropropanoates shows a rare bonding behavior with significant π character for the C=O_{coord} bond whereas the C-O_{pendant} bond is long and bears a basic function. Complex **1** serves as a metalloligand towards AgO₂CCF₂CF₃ to give PdAg(μ-O₂CCF₂CF₃)₂(O₂CCF₂CF₃-O)(dppf) **2**, which is fluxional in solution showing interchanges of the bridging and unidentate fluoropropanoate groups. Being an unusually stable Pd(II) carboxylate, **1** also serves an effective entry to mixed-metal carboxylates.

Introduction

Although carboxylate complexes have a long-standing history in coordination chemistry,¹ the coordination behaviour of carboxylates towards Pd(II) phosphine is poorly understood owing to the spontaneous decomposition of the system.² Even on rare occasions when such species were isolated,^{3–7} their chemical reactivity and dynamic behaviour were virtually unknown. The Pt(II) analogues on the other hand are stable and established.^{8,9} In this paper, we report a rare isolation and structural characterization of a representative in this system, Pd(O₂CCF₂CF₃)₂(dppf) **1**, and demonstrate that this *cis*-arrangement of two unidentate carboxylate groups^{7,9,10} is a powerful entity to enter into the field of heterobimetallic carboxylates.¹¹ This is exemplified by the isolation of a Ag(I)/Pd(II) bimetallic system, which is an extension of our recent interest in Ag(I) carboxylates.¹² While there are examples of bimetallic carboxylate systems,^{11,13,14} we are not aware of any reports on the preparation of a similar system using *cis*-oriented unidentate carboxylates as precursors.

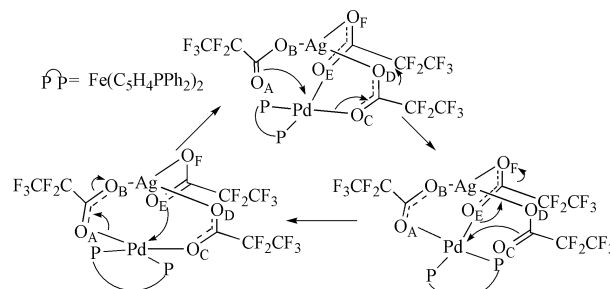
Results and discussion

Metathesis of PdCl₂(dppf) with two mole equivalents of AgO₂CCF₂CF₃ yields **1** in near-quantitative yield (95%). Excess AgO₂CCF₂CF₃ results in PdAg(μ-O₂CCF₂CF₃)₂(O₂CCF₂CF₃-O)(dppf) **2** as a byproduct. Complex **2** can be obtained from stoichiometric equivalents of **1** and AgO₂CCF₂CF₃ in good yield (*ca.* 88%), which lends support that **1** is the precursor of **2**. The IR symmetrical and antisymmetrical $\nu(\text{CO}_2^-)$ stretches of **1** at 1325 and 1688 cm⁻¹ respectively, with a difference ($\Delta\nu$) of 363 cm⁻¹, are consistent with a unidentate coordination mode for the carboxylate.¹⁵ The IR spectrum of **2** is more complex—it displays features of both unidentate [$\nu_{\text{antisym}}(\text{CO}_2^-)$ 1715 sh and 1690 vs cm⁻¹ and $\nu_{\text{sym}}(\text{CO}_2^-)$ 1326 m cm⁻¹] and bridging [$\nu(\text{CO}_2^-)$ 1586, 1574, 1436 and 1401 cm⁻¹] carboxylates. The NMR spectra give a significantly more deshielded phosphorus (δ_{P} 40.4) in **2** as compared to **1** (δ_{P} 36.5). This deshielding effect is also felt by the Cp and Ph ring protons of dppf (¹H NMR) and the fluorine nuclei (δ_{F} -7.73 and -43.90 for **1** and -7.54 and -43.01 for **2**).

The spectroscopic data suggest that the fluoropropanoate is in a unidentate mode in **1**. Crystallographic analysis reveals that it is mononuclear with chelating dppf and two unidentately coordinated fluoropropanoates. With AgO₂CCF₂CF₃, both pendant oxygens bind to the incoming metal thus forming two fluoropropanoate bridges in **2**. The third fluoropropanoate on the Ag(I) remains unidentate. This X-ray structure is not consistent with the ¹⁹F NMR spectrum which gives only one set of ¹⁹F peaks.

We have performed the ¹⁹F and ³¹P variable-temperature NMR experiments of **2** in CDCl₃. The former clearly shows the dynamics of the system in solution (Fig. 1). As shown, the two singlets, corresponding to CF₂ and CF₃, broaden as the temperature decreases. The CF₃ peak eventually splits into two with ratio 2 : 1 at 233 K. Some degree of selective line broadening is observed at the lower limit of the experiments (213 and 223 K), the CF₂ (at $\delta \approx 40$) shows non-symmetrical broadening. Deconvolution of the CF₂ peak at 223 K (Fig. 2a) and 213 K (Fig. 2b) shows that it comprises three peaks with similar intensities. Surprisingly, the CF₃ peaks do not show any significant broadening. The ³¹P NMR spectrum shows a single resonance at room temperature. It broadens and splits to two symmetric peaks at lower temperature (Fig. 3).

These spectral changes can be related to two independent fluxional mechanisms as depicted in Schemes 1 and 2. The unidentate and bridging fluoropropanoates interchange rapidly



Scheme 1 An interchange mechanism for unidentate and bridging fluoropropanoate of (dppf)Pd(μ-O₂CCF₂CF₃)₂Ag(O₂CCF₂CF₃-O) **2** in solution via exchange of the pendant oxygen and the oxygen atoms on palladium.

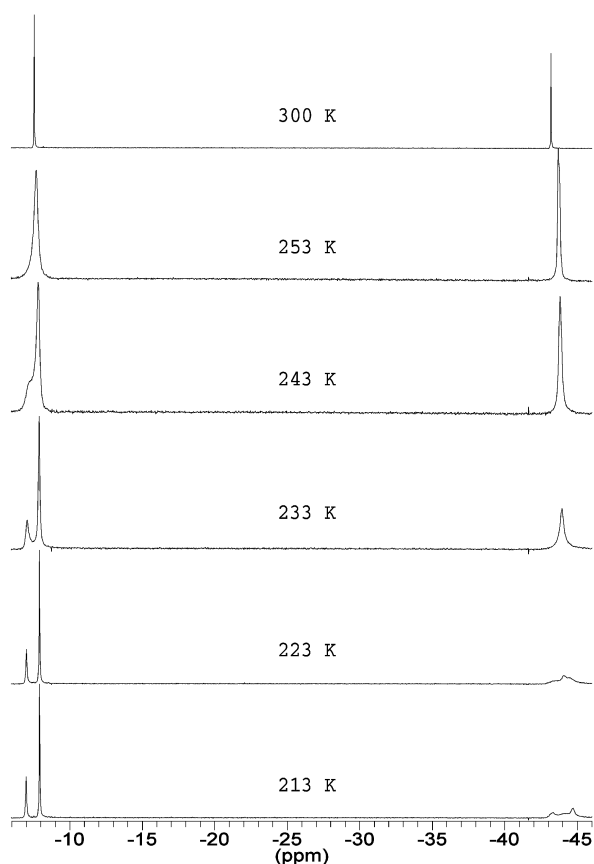


Fig. 1 VT ^{19}F NMR spectra of $\text{PdAg}(\mu\text{-O}_2\text{CCF}_2\text{CF}_3)_2(\text{O}_2\text{CCF}_2\text{CF}_3\text{-O})(\text{dppf})$ **2** in CDCl_3 .

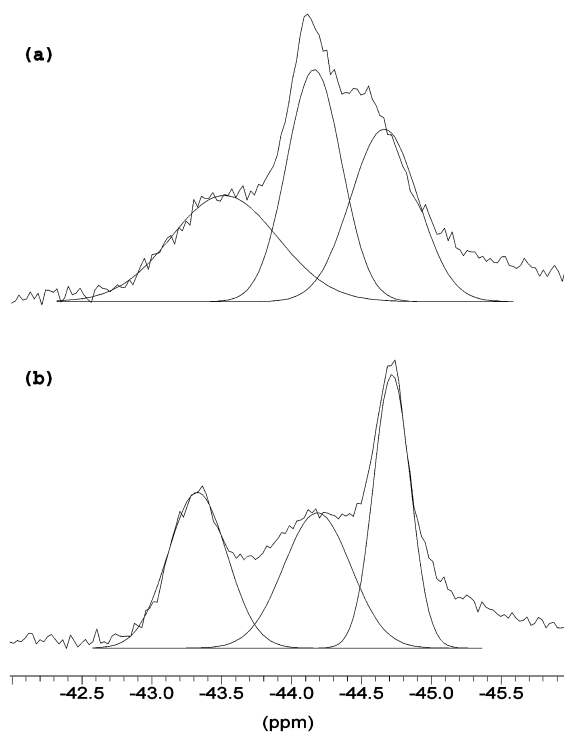


Fig. 2 Deconvoluted ^{19}F peaks of CF_2 of $\text{PdAg}(\mu\text{-O}_2\text{CCF}_2\text{CF}_3)_2(\text{O}_2\text{CCF}_2\text{CF}_3\text{-O})(\text{dppf})$ **2** in CDCl_3 at (a) 223 K and (b) 213 K.

through attack of the pendant oxygen on Pd, thereby releasing one of its attached carboxylate oxygens (Scheme 1). The displaced oxygen returns to Pd and the cycle repeats on each of the fluoropropanoates. Effectively, the Ag core rapidly tumbles around the Pd centre with a sequential Pd–O bond

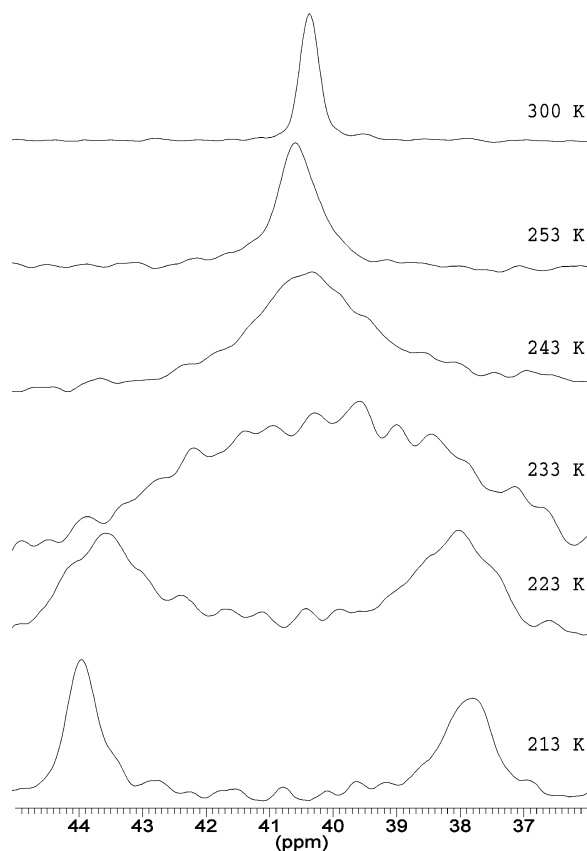
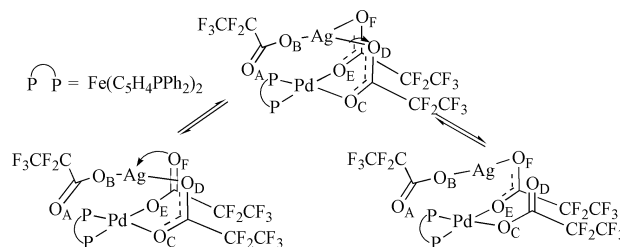


Fig. 3 VT ^{31}P NMR spectra of $\text{PdAg}(\mu\text{-O}_2\text{CCF}_2\text{CF}_3)_2(\text{O}_2\text{CCF}_2\text{CF}_3\text{-O})(\text{dppf})$ **2** in CDCl_3 .



Scheme 2 Rapid exchange of two- and three-coordinated $\text{Ag}(\text{I})$ of $(\text{dppf})\text{Pd}(\mu\text{-O}_2\text{CCF}_2\text{CF}_3)_2\text{Ag}(\text{O}_2\text{CCF}_2\text{CF}_3\text{-O})$ **2** in solution.

breaking/making that equilibrates all the fluoropropanoates. Below 243 K, this fluxionality slows down considerably, which results in splitting and separation of the ^{19}F peaks. The phosphorus atoms are indistinguishable at $\approx 253\text{--}300$ K, which corresponds to the solid state structure. The symmetric splitting of the ^{31}P peak at low temperatures could be rationalised by a facile exchange between two- and three-coordinate $\text{Ag}(\text{I})$ through making and breaking of Ag–O bonds (Scheme 2). This process does not require the exchange of bridging and terminal fluoropropanoates. The CF_3 signals of the bridging fluoropropanoates are less affected because they are further away from the migration sites. This exchange (Scheme 2) is understandably more rapid than that depicted in Scheme 1. These exchanges are expected to be retarded by the presence of another Lewis acid. When a molar equivalent of $\text{AgO}_2\text{CCF}_2\text{CF}_3$ is added to **2**, the product, tentatively assigned as $\text{PdAg}_2(\mu\text{-O}_2\text{CCF}_2\text{CF}_3)_2(\text{O}_2\text{CCF}_2\text{CF}_3\text{-O})(\text{dppf})$ **3** ($\delta_{\text{P}} 41.95$, $\delta_{\text{F}} -7.54$ and -43.01), does not show ^{31}P peak splitting at 213 K, although the CF_3 singlet splits neatly to two equal-intensity peaks (Fig. 4). The CF_2 signal broadens only at the lowest limit of the experiments.

In view of the rarity of stable $\text{Pd}(\text{II})$ phosphine carboxylates, their potential use as heterobimetallic precursors, and the solution dynamics, we have carried out single-crystal X-ray

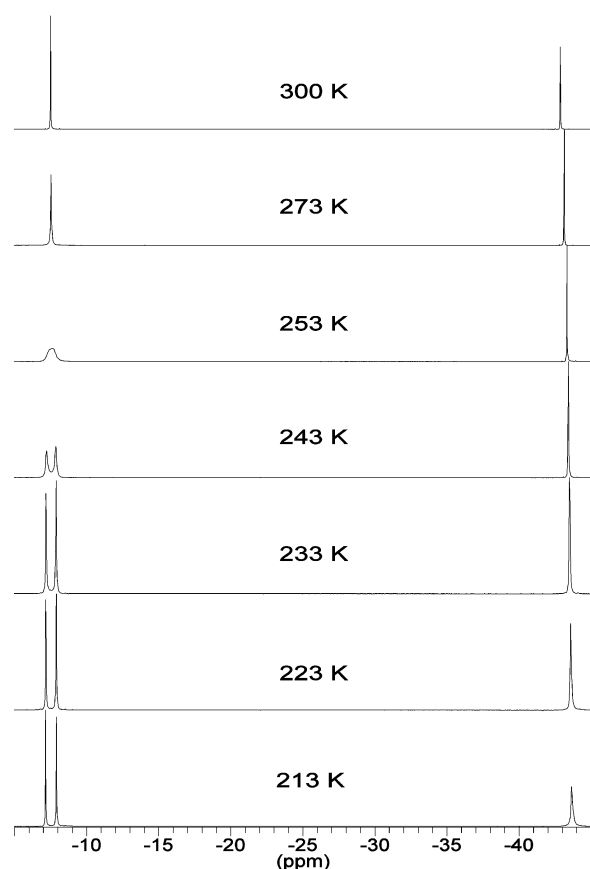


Fig. 4 VT ^{19}F NMR spectra of $\text{PdAg}_2(\mu\text{-O}_2\text{CCF}_2\text{CF}_3)_2(\text{O}_2\text{CCF}_2\text{CF}_3\text{-O})_2(\text{dppf})$ **3** in CDCl_3 .

crystallographic analysis of complexes **1** and **2** (Tables 1 and 2; Figs. 5 and 6). The results are consistent with the solution structures proposed above. It is notable that **1** prefers a mononuclear structure with chelating dppf and two *cis*-fluoropropanoates despite the fact that (a) bridging (and even ionic) carboxylates are much more common than unidentate carboxylates;¹ (b) the thermodynamic stability of the *cis*-arrangement of two unidentate carboxylates is much lower compared to other alternative arrangements; (c) carboxylate chains longer than C_1 usually prefer a chelating or bridging to a unidentate mode; (d)

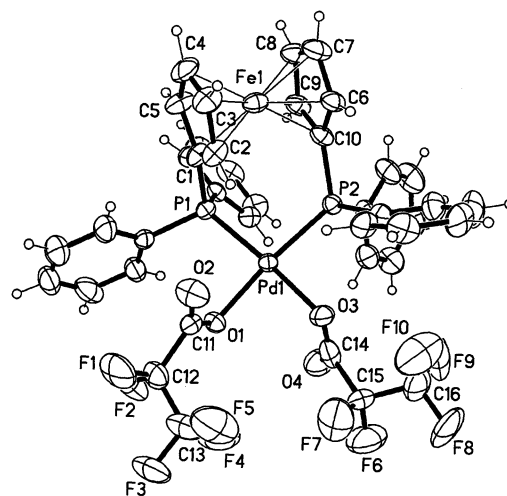
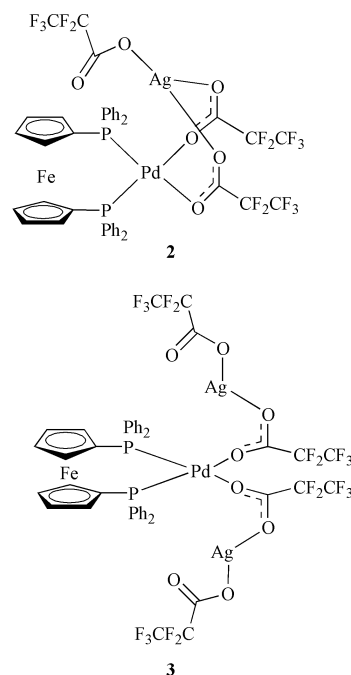


Fig. 5 ORTEP²⁵ drawing (50% probability ellipsoids) of the molecular structure of $\text{Pd}(\text{O}_2\text{CCF}_2\text{CF}_3)_2(\text{dppf})$ **1**.

Table 1 Crystallographic data and refinement details for **1** and **2**·2H₂O

	1	2 ·2H ₂ O
Chemical formula	$\text{C}_{40}\text{H}_{28}\text{F}_{10}\text{FeO}_4\text{P}_2\text{Pd}$	$\text{C}_{43}\text{H}_{32}\text{AgF}_{15}\text{FeO}_8\text{P}_2\text{Pd}$
M_r	986.81	1293.76
Temperature/K	223(2)	223(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
$a/\text{\AA}$	12.776(1)	11.809(1)
$b/\text{\AA}$	20.945(2)	13.747(1)
$c/\text{\AA}$	15.511(1)	14.955(1)
a°	90	83.046(1)
β°	110.990(2)	74.119(1)
γ°	90	82.730(1)
$V/\text{\AA}^3$	3875.2(5)	2306.77(4)
Z	4	2
$\rho_{\text{calcd}}/\text{g cm}^{-3}$	1.691	1.860
μ/mm^{-1}	1.001	1.298
Reflections collected	32140	13307
Independent reflections	11255 [$R(\text{int}) = 0.1131$]	9075 [$R(\text{int}) = 0.0238$]
GOF on F^2	0.824	1.095
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0565$, $wR_2 = 0.0817$	$R_1 = 0.0628$, $wR_2 = 0.1650$
R indices (all data)	$R_1 = 0.1192$, $wR_2 = 0.0930$	$R_1 = 0.0680$, $wR_2 = 0.1706$
$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}}/\text{e \AA}^{-3}$	0.902, -1.294	1.756, -1.699

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{\sum w[(F_o^2 - F_c^2)^2] / \sum wF_o^4\}^{1/2}.$$

Table 2 Selected bond distances (Å) and angles (°) of **1** and **2·2H₂O**. τ is the torsional angle of ferrocene while χ_A and χ_B are the centroids of the Cp rings of dppf

	1	2·2H₂O
Pd(1)–P(1)	2.2525(11)	2.2609(15)
Pd(1)–P(2)	2.2685(11)	2.2808(16)
Pd(1)–O(1)	2.076(3)	2.114(4)
Pd(1)–O(3)	2.065(3)	2.095(5)
Pd(1)–Ag(1)	—	3.0987(8)
C(11)–O(1)	1.272(5)	1.246(9)
C(11)–O(2)	1.197(5)	1.224(9)
C(14)–O(3)	1.201(6)	1.248(10)
C(14)–O(4)	1.245(6)	1.219(11)
Ag(1)–O(2)	—	2.249(6)
Ag(1)–O(4)	—	2.403(7)
Ag(1)–O(5)	—	2.164(6)
C(17)–O(5)	—	1.240(10)
C(17)–O(6)	—	1.214(10)
P(1)–Pd(1)–P(2)	96.38(4)	97.64(6)
O(1)–Pd(1)–O(3)	85.53(11)	86.5(2)
P(1)–Pd(1)–O(1)	90.03(8)	175.49(15)
P(1)–Pd(1)–O(3)	174.29(10)	89.46(15)
P(2)–Pd(1)–O(1)	173.59(8)	85.83(14)
P(2)–Pd(1)–O(3)	88.08(9)	164.43(16)
Pd(1)–O(1)–C(11)	113.6(3)	122.7(4)
Pd(1)–O(3)–C(14)	118.8(4)	127.9(5)
O(1)–C(11)–O(2)	129.4(4)	130.5(7)
O(3)–C(14)–O(4)	131.2(5)	130.8(7)
O(2)–Ag(1)–O(5)	—	153.7(2)
O(4)–Ag(1)–O(5)	—	117.0(2)
O(2)–Ag(1)–O(4)	—	87.5(3)
Ag(1)–O(5)–C(17)	—	116.5(5)
O(5)–C(17)–O(6)	—	128.2(8)
P(1)–Pd(1)–Ag(1)	—	98.23(4)
P(2)–Pd(1)–Ag(1)	—	109.86(5)
O(1)–Pd(1)–Ag(1)	—	83.22(14)
O(3)–Pd(1)–Ag(1)	—	82.61(15)
O(2)–Ag(1)–Pd(1)	—	74.19(15)
O(4)–Ag(1)–Pd(1)	—	75.54(15)
O(5)–Ag(1)–Pd(1)	—	119.26(16)
τ	–33.5	31.3
χ_A –Fe– χ_B	179.71	178.98

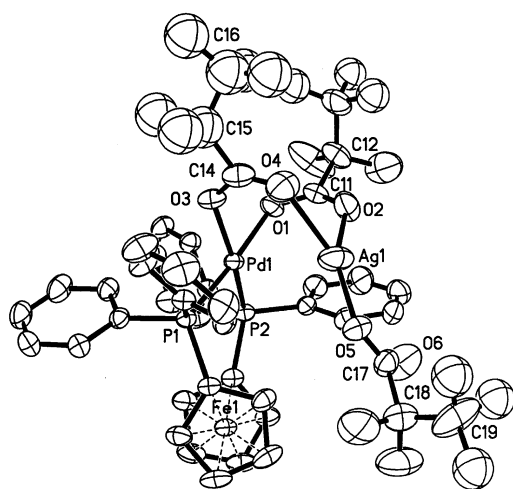


Fig. 6 ORTEP²⁵ drawing (50% probability ellipsoids) of the molecular structure of PdAg(μ -O₂CCF₂CF₃)₂(O₂CCF₂CF₃-O)(dppf)·2H₂O **2·2H₂O**. The hydrogen atoms, minor disordered F atoms and water solvates are omitted for clarity.

chelating dppf can easily convert to bridging dppf (in support of the changes in the mode of coordination of carboxylate) which is equally common.¹⁶ The near quantitative yield of **1** suggests that the synthesis is isomerically self-selective—there is no evidence of other coordination isomers (Fig. 7). Similar *cis*-arranged unidentate carboxylates are also observed in other

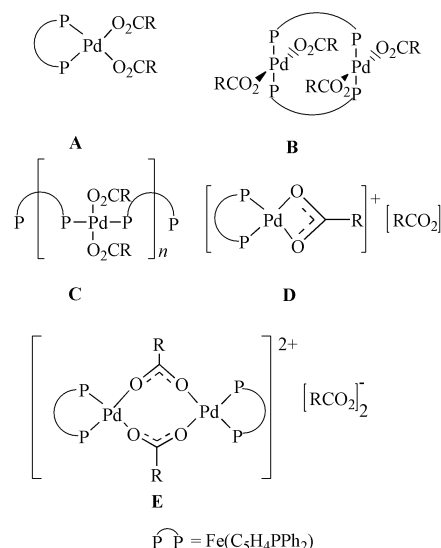


Fig. 7 Some possible coordination and geometric isomers of Pd(O₂CCF₂CF₃)₂(dppf) **1**.

square planar platinum group metal complexes, but most of them are spectroscopically identified,^{10,17} except a few notable exceptions that have crystallographic support.^{3,6,7,9,18} Based on IR data the AsPh₃ analogue of **1** has unidentate carboxylates.¹⁷

At first glance, the structure of **1** is similar to that of Pd(O₂CCF₃)₂(L) [L = dppm **4**,⁷ 6,6'-dimethoxybiphenyl-2,2'-diylbis(diphenylphosphine) **5**⁶]. Closer examinations revealed two notable differences: (a) the two pendant O atoms are in a *syn* conformation in **4** and **5** whereas in **1** they are *anti* to each other; (b) in a unidentate mode the C–O_{coord} is expected to be typically C–O single bonds (1.23⁷–1.295^{19c} Å)^{7,9,18a,19} whereas the C–O_{pendant} usually has a predominantly C=O π character (1.19^{7,19a}–1.23^{18a} Å).^{7,9,18a,19} This is observed in **4** and **5** but in **1**, only one of the two fluoropropanoates shows such character. The odd fluoropropanoate has a C–O_{pendant} [1.245(6) Å] bond that is significantly longer than the C–O_{coord} [1.201(6) Å] (Fig. 8). We are not aware of reports of such an anomaly in

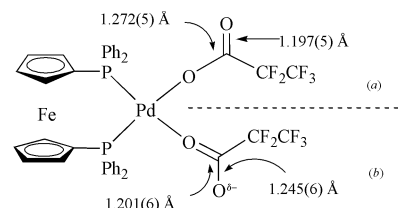


Fig. 8 Structure of Pd(O₂CCF₂CF₃)₂(dppf) **1** showing different bonding modes of the CF₃CF₂CO₂[–] groups: (a) shows the common unidentate carboxylate bonding mode while (b) shows the odd unidentate carboxylate bonding mode.

the literature, except perhaps in Hg(O₂CMe)(Ph)^{20†} which shows much smaller C–O bond distance differences (1.29 and 1.31 Å).²⁰ While the exact reason of such an anomaly is not clear, the intention seems reasonable—the complex uses this mechanism to transfer some charge away from the M–O to the C–O sites. This gives a more anionic and nucleophilic character to the C–O moiety *i.e.* –C–O^{δ–}, and renders the O_{coord} more like a neutral (and weaker) σ donor *i.e.* –C=O \rightarrow M. The higher charge on the pendant oxygen also forces the neighboring fluoropropanoate groups to minimize repulsion by adopting an *anti* conformation. This arrangement is in line with the steric effect imposed by dppf. The dissipation of charge away from the metal appears to support an internal redox mechanism

[†] As the Hg–O_{pendant} distance (2.85 Å)²⁰ appears too short to be ignored, it may be considered as a semi-chelate instead of a typical unidentate mode as in **1** (Pd \cdots O_{pendant} 3.156 Å).

recognized in Pd(II) phosphine carboxylates. These are active catalytic precursors because of their ability to give Pd(0) species spontaneously without the need to introduce an external reducing agent. The transformation of an acyloxy to a carbonyl group appears to provide an avenue for the Pd in its formal oxidation state (+2) to stabilize itself without going through a self-destructive reduction process. With such a coordination mode, the two phosphorus nuclei are strictly inequivalent in a static state. This is not consistent with the singlet observed in the rt spectrum. At lower temperatures, the ^{31}P NMR spectrum (Fig. 9) shows an emerging pair of doublets (δ_{P} 40.4 and 35.1;

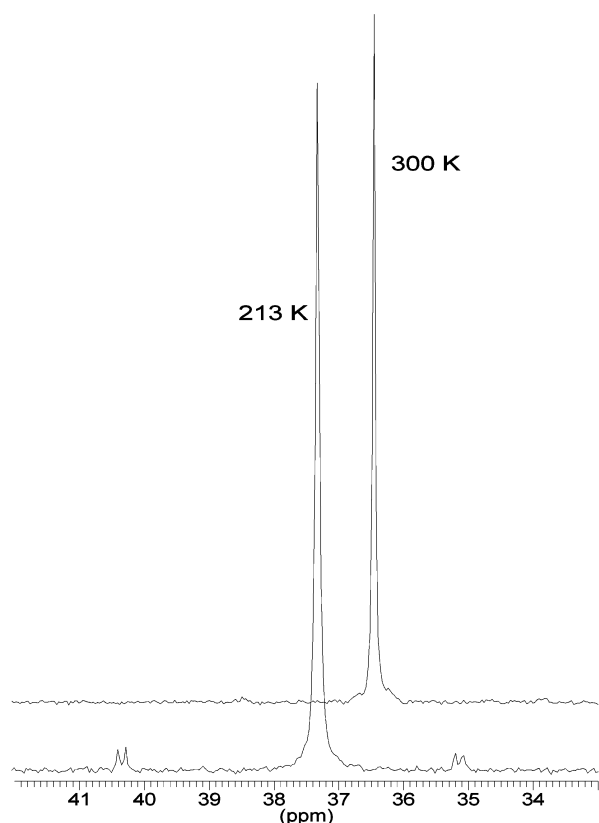
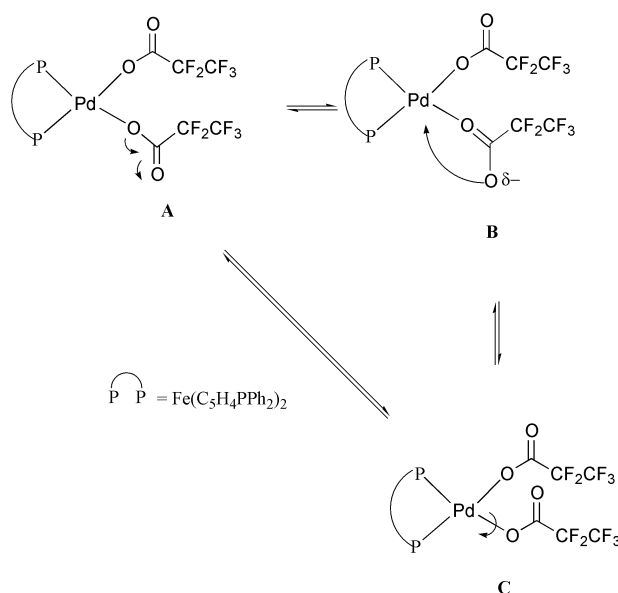


Fig. 9 VT ^{31}P NMR spectra of $\text{Pd}(\text{O}_2\text{CCF}_2\text{CF}_3)_2(\text{dppf})$ **1** in CDCl_3 .

$^2J_{\text{PP}} = 15.25$ Hz) with a small coupling constant consistent with *cis*-coupling. At the limit of the experiments, these doublets are still weak compared to the singlet. Similar observations are recorded in the CF_2CF_3 peaks in ^{19}F NMR spectra at lower temperatures. These point to a slow emergence of a static structure with phosphine and carboxylates inequivalent (**B** in Scheme 3). A reasonable fluxionality would involve the carboxylate fluctuating between *syn* and *trans*-conformations (of the pendant oxygen) in solution. This can proceed *via* free rotation of Pd–O bonds and nucleophilic attack of pendant oxygen on the Pd centre (Scheme 3). The single-crystal X-ray structure of **1** is also consistent with an “intermediate” mode (**B**) of the process (Scheme 3).

The nucleophilic character of the pendant O enables **1** to “mop up” $\text{AgO}_2\text{CCF}_2\text{CF}_3$ readily. The resultant **2** shows a bimetallic structure with two *syn-syn* bridging and one unidentate fluoropropanoate group. The coordination to $\text{AgO}_2\text{CCF}_2\text{CF}_3$ weakens slightly both Pd–P [av. 2.2709(16) Å] and Pd–O [av. 2.105(5) Å] bonds in **2** as compared with **1** [Pd–P: av. 2.2605(11) Å. Pd–O: av. 2.071(3) Å]. The weaker Pd–O bonds could provide a pathway for facile carboxylate interchange to occur, which requires the cleavage of the Pd–O bond as a key step. The two Ag–O(bridging) bonds are significantly different [2.249(6) and 2.403(7) Å]. With the mobility of both fluoropropanoate restricted, some angular distortions are apparent. For example, the two *trans*-P–Pd–O angles [175.49(15) and 164.43(16)°] differ



Scheme 3 Rapid tumbling of a unidentate fluorocarboxylate through exchange of a pendant and coordinated oxygen of $\text{Pd}(\text{O}_2\text{CCF}_2\text{CF}_3)_2(\text{dppf})$ **1** in CDCl_3 .

significantly by $>10^\circ$, whereas for **1** they are essentially equal [174.29(10) and 173.59(8)°]. The Ag(I) geometry is planar but tends towards a T than a trigonal shape. The Pd–Ag distance [3.0987(8) Å], which is shorter than the van der Waals contact of Pd–Ag (3.30 Å), is brought about by the two bridging fluoropropanoates rather than formal M–M interactions.

Isolation of **1** clearly suggests that under favourable conditions, some Pd(II) phosphine carboxylates are stable enough to be isolated and studied. This has positive implications in the design of Heck-type catalysts. The use of fluoro derivatives helps the cause by stabilizing the unidentate mode, without nullifying its basicity. This delicate balance helps **1** capture other Lewis acidic fragments such that formation of species like **2** is realized. Such a balance of stability, catalytic activity and chemical reactivity poses a prime challenge to the design of many catalytic systems. Our immediate task is to look for other bimetallic complexes that could expand the horizon of Heck-type syntheses, which are almost exclusively Pd(II) based. We are also interested to explore the catalytic activities of **2** which is sufficiently basic to react with excess $\text{AgO}_2\text{CCF}_2\text{CF}_3$. This opens an extra window for us to enter the field of mixed-metal mixed-carboxylates.

Experimental

General procedures

All reactions were performed under pure dry argon using standard Schlenk techniques. The products are stable and hence recrystallizations were performed in air. All solvents and reagents were of reagent grade obtained from commercial sources and used without further purification. $\text{PdCl}_2(\text{dppf})$ was prepared following the literature method.²¹

All ^1H , ^{31}P and ^{19}F NMR spectra were recorded at ca. 300 K at operating frequencies of 299.96, 121.49 and 282.23 MHz respectively. ^1H , ^{31}P and ^{19}F chemical shifts are quoted in ppm downfield of Me_4Si , and external $\text{CF}_3\text{CO}_2\text{H}$ and 85% H_3PO_4 respectively. All IR spectra were recorded in the solid state on a Bio-Rad FT-IR spectrometer using a KBr disk. Elemental analyses were performed by the Elemental Analysis Laboratory of our Department.

Syntheses

Synthesis of $\text{Pd}(\text{O}_2\text{CCF}_2\text{CF}_3)_2(\text{dppf})$ **1.** $\text{PdCl}_2(\text{dppf})$ (0.400 g, 0.547 mmol) and $\text{AgO}_2\text{CCF}_2\text{CF}_3$ (0.2977 g, 1.099

mmol) in CH_2Cl_2 (80 cm^3) were stirred at rt, shielded from direct light for ca. 20 h. The dark red suspension was filtered through a column of Celite, giving a deep red filtrate which was concentrated to ca. 10 cm^3 . Hexane was added to crystallize the compound, complex **1** (Yield, 0.5143 g, 95%). (Found: C, 48.68; H, 2.52%. $\text{C}_{40}\text{H}_{28}\text{F}_{10}\text{O}_4\text{P}_2\text{Pd}$ requires C, 48.40; H, 2.86%). $\nu_{\text{max}}/\text{cm}^{-1}$ (RCO_2^-) 1688 vs and 1325 s (KBr); δ_{H} (CDCl_3) 4.44 [4 H, d, $^3J(\text{PH})$ 1.6 Hz, C_5H_4]; 4.50 (4 H, s, C_5H_4); 7.36–7.42 (8 H, m, Ph); 7.50–7.56 (4 H, m, Ph) and 7.77–7.85 (8 H, m, Ph); δ_{P} (CDCl_3) 36.48 (s); δ_{F} (CDCl_3) –7.73 (6 F, s, CF_3) and –43.90 (4 F, s, CF_2).

Synthesis of $\text{PdAg}(\mu\text{-O}_2\text{CCF}_2\text{CF}_3)_2(\text{O}_2\text{CCF}_2\text{CF}_3\text{-O})(\text{dppf})$ **2.** $\text{AgO}_2\text{CCF}_2\text{CF}_3$ (0.0166 g, 0.0613 mmol) was added to a solution of $\text{Pd}(\text{O}_2\text{CCF}_2\text{CF}_3)_2(\text{dppf})$ **1** (0.0600 g, 0.0608 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred for 30 min, shielded from direct light. The mixture was then filtered to remove the insoluble Ag particles. Purplish black coloured crystals of **2**· $2\text{H}_2\text{O}$ were collected (0.0692 g, 88%) after slow diffusion of the filtrate through a layer of hexane with shielding from direct light. (Found: C, 39.44; H, 2.09%. $\text{C}_{43}\text{H}_{32}\text{AgF}_{15}\text{FeO}_8\text{P}_2\text{Pd}$ requires C, 39.92; H, 2.49%). $\nu_{\text{max}}/\text{cm}^{-1}$ (RCO_2^-) 1715 sh, 1690 vs, 1586 m, 1574 m, 1436 s, 1401 s and 1326 m (KBr); δ_{H} (CDCl_3) 4.54 (4 H, s, C_5H_4); 4.61 (4 H, s, C_5H_4); 7.44–7.48 (8 H, m, Ph); 7.56–7.61 (4 H, m, Ph) and 7.82–7.89 (8 H, m, Ph); δ_{P} (CDCl_3) 40.44 (s); δ_{F} (CDCl_3) –7.54 (9 F, s, CF_3) and –43.01 (6 F, s, CF_2).

Synthesis of $\text{PdAg}_2(\mu\text{-O}_2\text{CCF}_2\text{CF}_3)_2(\text{O}_2\text{CCF}_2\text{CF}_3\text{-O})_2(\text{dppf})$ **3.** $\text{PdAg}(\text{O}_2\text{CCF}_2\text{CF}_3)_3(\text{dppf})\cdot 2\text{H}_2\text{O}$ (0.050 g, 0.0386 mmol) and AgO_2CETf (0.0108 g, 0.0386 mmol) were allowed to stir in CH_2Cl_2 (20 cm^3) for 30 min, shielded from direct light. The reaction mixture was then dried *in vacuo*. The product **3** was recrystallized in CH_2Cl_2 –hexane. Yield, 0.053 g (87%). (Found: C, 36.19; H, 1.90%. $\text{C}_{46}\text{H}_{28}\text{Ag}_2\text{F}_{20}\text{FeO}_8\text{P}_2\text{Pd}$ requires C, 36.14; H, 1.85%). $\nu_{\text{max}}/\text{cm}^{-1}$ (RCO_2^-) 1681 vs, 1635 sh, 1575 w, 1558 w, 1481 m, 1436 s, 1409 s, 1327 vs (KBr); δ_{H} (CDCl_3) 4.56 (4 H, s, C_5H_4); 4.64 (4 H, s, C_5H_4); 7.44–7.52 (8 H, m, Ph); 7.56–7.61 (4 H, m, Ph) and 7.82–7.90 (8 H, m, Ph); δ_{P} (CDCl_3) 41.95 (s); δ_{F} (CDCl_3) –7.54 (12 F, s, CF_3) and –43.01 (8 F, s, CF_2).

Crystal structure determinations

The diffraction experiments were carried out on a Bruker SMART CCD diffractometer with a Mo-K α sealed tube at –50 °C. The program SMART²² was used for collecting frames of data, indexing reflections and determination of lattice parameters, SAINT²² for integration of the intensity of reflections and scaling, SADABS²³ for absorption correction and SHELXTL²⁴ for space group and structure determination and least-squares refinements on F^2 . The relevant crystallographic data and refinement details are shown in Table 1. Compound **2** crystallized with two molecules of H_2O and the F atoms are severely disordered. The three F atoms attached to C(13) were found to be disordered. Two disorder models (occupancies 0.6 and 0.4) were resolved and included in the least-squares refinement cycles. Individual isotropic thermal parameters were refined for the F atoms with occupancies 0.6 and a common isotropic thermal parameter was refined for the minor component. Two independent orientations were found for one CF_2 – CF_3 group [attached to C(14)] with occupancies 50 : 50. Common isotropic thermal parameters were refined for these disordered atoms. The F atoms attached to C(19) were disordered. Two orientations of F atoms were included in the model. Of the two water molecules found in the lattice, one was disordered with an occupancy of 50 : 50.

CCDC reference numbers 165079 and 165080.

See <http://www.rsc.org/suppdata/dt/b1/b104539n/> for crystallographic data in CIF or other electronic format.

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