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Isolation and structural characterization of some stable Pd(II) carboxylate complexes supported by 1,1'-bis(diphenylphosphino)ferrocene (dppf)

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Abstract

Although catalytically active palladium phosphine carboxylates are generally unstable, a series of such complexes are stabilized by dppf, viz. Pd(O₂CR)₂(dppf) [R = CF₃ **I**, CF₂CF₃ **II** [1,43] CF₂CF₂CF₃ **III**, CHCl₂ **IV**, *o*-C₆H₄Cl **VI**, CH₂CO₂H **VII**, CH=CHCO₂H **VIII**]. They have been spectroscopically characterized and their structures determined by X-ray single-crystal crystallography. Two derivatives viz. Pd(O₄C₂-*O,O'*)(dppf) **IX** and PdCl(O₂CPh)(dppf) **X** are included for comparison. They are invariably mononuclear with chelating phosphine and unidentate carboxylates. The more labile (and less basic) carboxylates tend to form complexes that are more resistive to reductive decomposition. Pd(O₂CPh)₂(dppf) **V** decomposes readily to PdCl₂(dppf) in the presence of chlorinated solvents. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Carboxylate; Structures; Phosphine; Heck catalyst; Ferrocenyl phosphine

1. Introduction

Although carboxylate complexes are well documented and generally stable [2], there are notable exceptions such as Pd(II) phosphine carboxylates, which are mostly unisolable. These are important complexes as they serve as precursors in many palladium-catalyzed organic reactions [3,4], such as the Heck-type syntheses [3,5–11]. It is generally believed that they undergo spontaneous decompositions to Pd(0) species [6,12] that are responsible for the catalytic activities [3–6,12]. The mode of decomposition, the intermediates and final products are, perhaps not surprisingly, complex and a matter of much debate. For example, the coordination chemistry of a possibly key intermediate like [Pd(PR₃)₃(OAc)]⁻ [12] is ill developed. To add to the confusion, studies by Ozawa and Hayashi showed that

such system is water-sensitive, and the catalytic activities are enhanced with the addition of water [6], and Herrmann et al. proposed the formation of Pd(IV) in the palladacycles in Heck Olefination [5]. The complexity is aggravated when definitive structural information of Pd(II) phosphine carboxylates is generally unavailable. Some carboxylate-like complexes are, however, emerging [17,18]. Spectroscopic data tend to give rise to conflicting results. For example, [Pd(O₂CR)₂(PR₃)₂] is generally accepted to be mononuclear with both carboxylates in an unidentate mode while [Pd(O₂CR)₂(PR₃)₂] is binuclear with bridging and unidentate carboxylates [13,14]. The former was earlier reported to be a *trans*-complex [15] but more recent reports appeared to suggest a *cis*-configuration [16]. However, both *cis* and *trans*-Pd(O₂CPh)₂(PPh₃)₂ seem to form the reaction of Pd(PPh₃)₄ with dibenzyl peroxide [19], Jutand's reports assume a *trans* geometry [12]. Although Pd(II) carboxylates are generally trimeric with bridging carboxylates [20,21], most reported Pd(II) phosphine carboxylates complexes are monomeric with unidentate carboxylates [1,13,15,19,22–27], except for example

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trans-[Pd(O₂CMe)₂(dbpp)]₄ [28] [dbpp = 1,3-bis(di-*tert*-butylphosphino)propane] which has a Pd₄ tetrameric core. The reasons for these variations are not well known. The outcome is also not easily predictable because carboxylates [2,29] and diphosphines commonly adopt a bridging or chelating mode.

We are particularly interested in the study of the interplaying influence of structure, nature of carboxylates and stability of these complexes. Such factors determine the catalytic value of these complexes and cast light on the formation pathway and products of the catalytically active species, so that a clear understanding is of help in the design of suitable precursors. Ideally, such complexes should be chemically stable and yet catalytically potent. As a follow up to our recent report [1] of Pd(O₂CCF₂CF₃)₂(dppf) and PdAg(O₂CCF₂CF₃)₃(dppf), we herein report other related complexes that we have isolated and characterized, viz. Pd(O₂CR)₂(dppf) [R = CF₃ **I**, CF₂CF₂CF₃ **III**, CHCl₂ **IV**, Ph **V**, *o*-C₆H₄Cl **VI**, CH₂CO₂H **VII**, CH=CHCO₂H **VIII**, Pd(O₄C₂)(dppf) **IX** and PdCl(O₂CR)(dppf) [R = Ph **X**, CF₃ **XI**]. The dppf ligand is the diphosphine of choice because of its catalytic value [30] and its ability to form stable chelates such that the carboxylates are juxtaposed to be *cis*.

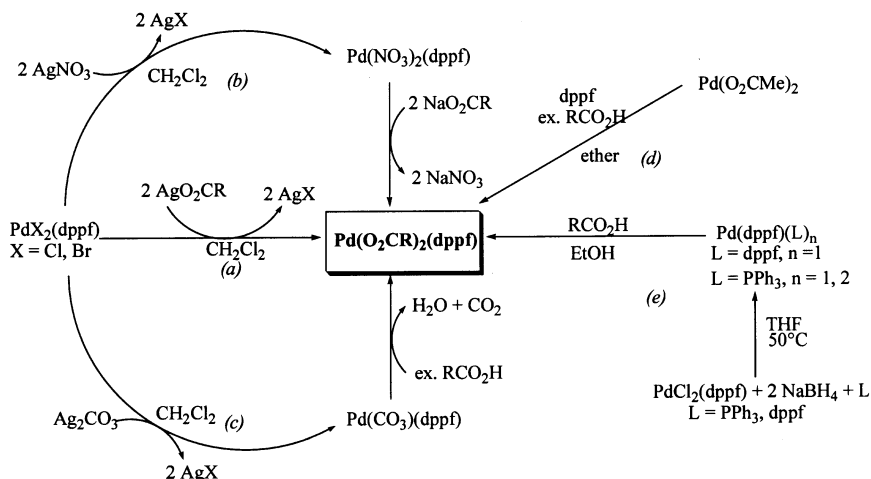
2. Results and discussion

The preparation of Pd(II) phosphine carboxylates can generally be accomplished with moderate to good yield from metathesis of Pd(II) phosphine halides with Ag(I) carboxylates (Scheme 1a) [14,31]. This is generally the preferred method due to good yield and simplicity. Similar attempts using alkali metal carboxylates would leave the Pd(II) complexes largely unreacted. An effective alternative is a two-step process by using Ag_nX (X = NO₃⁻, n = 1; X = CO₃²⁻, n = 2 [32]) in the metath-

esis, followed by attack by an alkali metal carboxylate (Scheme 1b) or carboxylic acid (Scheme 1c) to facilitate displacement. Other viable pathways include a direct attack of phosphines on the binary Pd(II) acetate trimer in the presence of excess carboxylic acid (Scheme 1d) [22] or oxidative reaction of carboxylic acid with Pd(0) phosphine complexes (Scheme 1e) [19,33]. Using this multitude of approaches, we have synthesized a series of Pd(II) phosphine carboxylates **I–XI**.

The IR and NMR spectroscopic data of these compounds are given in Table 1. The strong IR bands gave the first indication of the presence of the carboxylate group. The >200 cm⁻¹ difference (Δν) of symmetric and antisymmetric CO₂⁻ stretches is a useful [34], although not definitive [35] indication of unidentate mode for the ligand.

Although most of the Pd(O₂CR)₂(dppf) complexes have the Δν expected for unidentate carboxylate, there are a few cases that merit comment. Two sets of ν(CO₂⁻) vibrations are registered in **VII** and **VIII**. For **VII**, one [Δν 253 cm⁻¹ (1729 and 1476 cm⁻¹)] would suggest a unidentate group while the other [Δν 184 cm⁻¹ (1584 and 1400 cm⁻¹)] would favor a free acid assignment [34,35]. The integrated signal of methylene group in ¹H-NMR spectrum shows that there are four methylene protons per dppf unit. These point to the formulation of Pd(O₂CCH₂CO₂H)₂(dppf). The ¹H-NMR spectrum of **VIII** shows only one signal for CH=CH group, which is inconsistent with the crystallographic formulation of Pd(O₂CCH=CHCO₂H)₂(dppf) (see below). Low temperature ¹H- and ³¹P-NMR spectra do not show significant differences, except that the carboxylic acid proton peak (δ 16.47 ppm) is stronger. These point to a facile fluxionality equilibrating the two ends of olefinic group, e.g. via an exchange of the coordinated and pendent carboxylates. For the oxalate complex **IX**, the ν(C–O) stretches are comparable with those in K₂[Pd(O₄C₂)₂]·2H₂O (1698, 1675, 1657 and



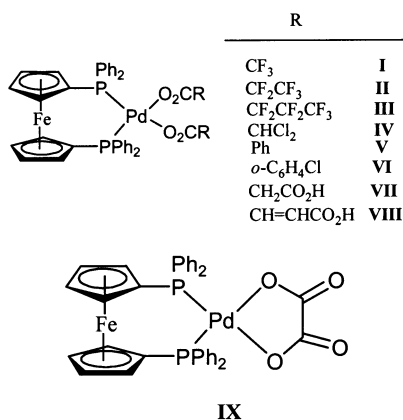
Scheme 1. Various synthetic pathways of Pd(II) phosphine carboxylates.

Table 1
Spectroscopic data

Complex	ν_{\max} (cm ⁻¹) (CO ₂ ⁻)	δ_{H} (ppm)	δ_{P} (ppm)
I	1716 s, 1689 s, 1402 m	4.46 (q, Cp, 4H); 4.52 (d, Cp, 4H); 7.39–7.45 (m, Ph, 8H); 7.53–7.58 (m, Ph, 4H); 7.77–7.85 (m, Ph, 8H)	36.2 (s)
II [1]	1688 vs, 1325 m	4.44 (d, Cp, 4H); 4.50 (s, Cp, 4H); 7.36–7.42 (m, Ph, 8H); 7.50–7.56 (m, Ph, 4H); 7.77–7.85 (m, Ph, 8H)	36.5 (s)
III	1684 vs, 1332 s	4.44 (s, Cp, 4H); 4.49 (s, Cp, 4H); 7.36–7.42 (m, Ph, 8H); 7.50–7.58 (m, Ph, 4H); 7.77–7.85 (m, Ph, 8H)	36.6 (s)
IV	1655 vs, 1637 sh, 1334 s	4.45 (s, Cp, 4H); 4.49 (s, Cp, 4H); 5.36 (s, CHCl ₂ , 2H); 7.38–7.48 (m, Ph, 8H); 7.48–7.65 (m, Ph, 4H); 7.80–7.92 (m, Ph, 8H)	35.6 (s)
V	1607 s, 1569 s, 1345 vs	4.45 (s, Cp, 4H); 4.52 (s, Cp, 4H); 7.11–7.70 (m, Ph, 12H); 7.91–7.98 (m, Ph, 8H)	33.5 (s)
VI	1622 vs, 1589 sh, 1355 vs	4.46 (s, Cp, 4H); 4.49 (s, Cp, 4H); 6.88–6.98 (m, C ₆ H ₄ Cl, 2H); 7.01–7.22 (m, C ₆ H ₄ Cl, 6H); 7.31–7.48 (m, Ph, 12H); 7.92–8.02 (m, Ph, 8H)	33.9 (s)
VII	1729 vs, 1584 vs, 1476 vs, 1400 s	2.52 (s, CH ₂ , 4H); 4.48 (q, Cp, 4H); 4.53 (d, Cp, 4H); 7.40–7.50 (m, Ph, 8H); 7.56–7.63 (m, Ph, 4H); 7.78–7.87 (m, Ph, 8H)	34.5 (s)
VIII	1708 s, 1623 s, 1578 s, 1384 s, 1336 s	4.48 (s, Cp, 4H); 4.68 (s, Cp, 4H); 5.79 (s, CH=CH, 4H); 7.40–7.50 (m, Ph, 8H); 7.55–7.61 (m, Ph, 4H); 7.78–7.88 (m, Ph, 8H); 16.47 (s broad, CO ₂ H, 1.2H)	35.0 (s)
IX	1698 s, 1676 vs, 1608 m, 1363 s	4.33 (s, Cp, 4H); 4.51 (s, Cp, 4H); 7.41–7.52 (m, Ph, 8H); 7.54–7.63 (m, Ph, 4H); 7.72–7.83 (m, Ph, 8H)	36.4 (s)

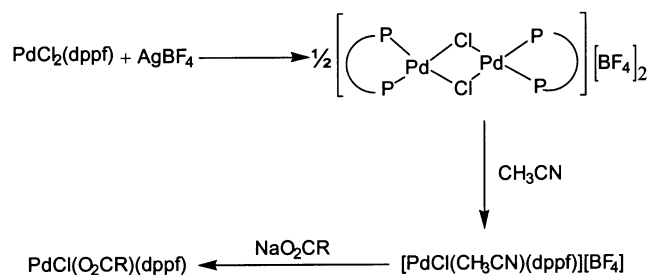
IR was recorded in KBr and NMR in CDCl₃

1394 cm⁻¹) [34], and hence are consistent with a chelating oxalate complex, viz. Pd(O₄C₂)(dppf).



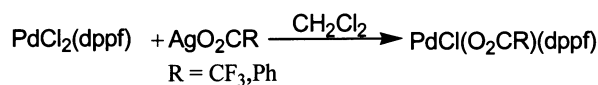
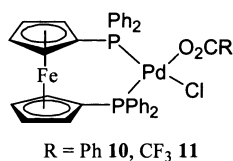
³¹P-NMR analysis of all complexes suggested that both phosphorus sites on dppf are chemically equivalent. The order of coordination shift (δ_{P}) generally follows the basicity of the carboxylate groups—the stronger the electron-withdrawing ability of the carboxylate, the poorer its basicity and the larger is the coordination shift [nucleophilicity (RCO₂⁻): Ph > *o*-C₆H₄Cl > CH₂CO₂H > HO₂CCH=CH > CHCl₂ > CF₃ > CF₃CF₂ > CF₃CF₂CF₂]. The more electronegative carboxylates accept electron density from Pd, either by inductive or mesomeric effect, which effectively removes the charge from phosphine ligands. The δ_{P} of the oxalato complex **IX**, is significantly higher than those complexes that have carboxylates of comparable nucleophilicity. This is expected since the oxalate, unlike the others, is chelating. Such a coplanar Pd(II) bis(chelate) structure should promote electron donation from the phosphine.

Attempts to synthesize **V** from the metathesis of PdCl₂(dppf) with two molar equivalence of AgO₂CPh in CH₂Cl₂ failed, leading only to the recovery of starting material PdCl₂(dppf). Our observations suggested that compound **V** indeed formed, but is too unstable to be isolated. This formation of **V** is supported with evidence; (i) when only one equivalent of AgO₂CPh was used, PdCl(O₂CPh)(dppf) **X** was isolated together with **V** and starting material PdCl₂(dppf). This shows that AgO₂CPh is able to cleave Pd–Cl bond. This is substantiated by the ³¹P-NMR spectrum (same sample) taken a few days later, that showed diminishing signal of **V** and increasing signal of PdCl₂(dppf). (ii) Similar attempts of synthesizing **V** from the metathesis of PdBr₂(dppf) with two molar equivalence of AgO₂CPh also results in recovery of the solvent-induced decomposition product PdCl₂(dppf). Its instability and decomposition are possibly related to those of Pd(O₂CCH₃)₂(PPh₃)₂, which has been well studied by Jutand et al. [12]. Such instability in fact is an encouraging sign that the complex is catalytically active as it readily releases the highly reactive Pd(0) moiety. Such moiety, under the current experimental conditions and in the presence of CH₂Cl₂ would generate PdCl₂(dppf) and release benzoic acid, which has been verified by EI/MS analysis of the product mixture. The stability of Pd(II) phosphine carboxylates is clearly dependent on the nucleophilicity of the carboxylates. The more nucleophilic CH₃CO₂⁻ and PhCO₂⁻ generate complexes that reduce readily in solution. The spectra are usually contaminated by decomposition products and such complexes are rarely chemically pure. Slightly less basic carboxylates like *o*-C₆H₄ClCO₂⁻ can support complexes like **VI**, which can be stable enough for spectroscopic

Scheme 2. Synthesis of PdCl(O₂CR)(dppf) via [Pd₂Cl₂(dppf)₂][BF₄].

and chemical analyses but they tend to decompose slowly in solution, which makes it difficult to obtain good single-crystals for X-ray diffraction study. The complex **IX** comprising C₂O₄²⁻ is significantly more stable than **VI**, but still decomposes in solution upon prolonged standing. Those with least basic carboxylates like dichloroacetate (in **IV**), hydrogen malonate (in **VII**), hydrogen maleate (in **VIII**), and fluorocarboxylates (in **I–III**) are the most stable in this series. To illustrate this further, we have examined the stability of **1** (δ_{P} 36.2 ppm) in CDCl₃ by NMR over a period of 7 weeks. It shows a gradual emergence of PdCl(O₂CCF₃)(dppf) **XI** (δ_{P} 33.8 and 38.8 ppm), suggesting the lability of the fluoroacetate and facile chlorine abstraction from the chlorinated solvent. Similar observations have been reported on the Pt(II) analogues in the presence of phosphine, although the decomposition tends to be faster [38]. Similarly, about 10% of the fluorobutanoate complex **III** would convert to the mixed chloro-carboxylato complex after ca. 60 h in CH₂Cl₂.

Such decomposition from bis-carboxylato complexes is rarely synthetically significant because of the low yields of the products and the difficulty in purification. However, the chloro monocarboxylate products are important compounds as they could provide a ready access to mixed-carboxylates, which are not easily accessible, and other monocarboxylate mixed-ligand systems. In view of this, we have developed two synthetic routes of **X** and **XI** viz. via [Pd₂(μ-Cl)₂(dppf)₂][BF₄]₂ [42] (Scheme 2), and directly from PdCl₂(dppf) using heterogeneous conditions (Scheme 3). The mixed ligand complex **X** is significantly more stable than pure carboxylate analog **V**. The large difference between the carboxylate symmetric and antisymmetric stretches is indicative of unidentate coordination. The ³¹P-NMR spectrum points to an asymmetric *cis*-phosphorus entity (**X**: δ_{P} 38.64 and 30.08 ppm; ²J_{P-P} 8 Hz).

Scheme 3. Hetero-mixture of PdCl(dppf) and AgO₂CR leading to mixed-ligand complexes.

In view of the rarity of crystallographically identified Pd(II) phosphine carboxylates and to gain a better understanding of the structural–stability relationship of these complexes, we have carried out single-crystal X-ray crystallographic analyses of compounds **I**, **II**, [1] **III**, **IV**, **VIII** and **X**. The analyses confirmed that all are mononuclear square-planar Pd(II) complexes. All except **X** have two carboxylates *cis* to each other (Tables 2 and 3; ORTEP drawing of **VIII** is shown in Fig. 1) whereas **X** is a mixed halo-carboxylato complex (Fig. 2), that crystallized as a solvate, **X**·CH₂Cl₂. It proved that bridging dppf, although common elsewhere, does not occur in this system.

One would expect that in a typical unidentate carboxylate, the C–O lengths are unequal and that the pendant carboxyl should be significantly stronger. Interestingly, even though the C–O_{coord} bond length in **1** [1.258(4) Å mean] are comparable with those in Pt(O₂CCF₃)₂(dppm) [1.259(9) Å mean] [36], the C=O_{free} bond lengths are longer [**1**: 1.206(4) Å mean; Pt(O₂CCF₃)₂(dppm): 1.193(9) Å mean] [36]. This appears to support our earlier theoretical calculation [36] that a more electronegative Pd(II), compared with Pt(II), would deplete the electron density on the pendant carboxyl group. Complex **VIII** is particularly interesting because of the added functionality of a carboxylic acid at the distal end of each carboxylate. Chemically, there is an extra dimension for the development of mixed-metal carboxylates. Catalytically, the higher solubility in aqueous system makes it more attractive for Heck-type reactions in water. The difference in the C–O lengths (C–O_{coord}–C=O_{free}) of the carboxylate (average 0.019 Å) is significantly smaller than the usual difference of greater than 0.04 Å found in similar complexes. This is attributed to the intramolecular and intraligand H-bonding between the carboxylic acid proton and the carboxylate oxygen (1.765 and 1.804 Å). This internal H-bond is also observed in its ¹H-NMR spectrum (δ_{H} 16.47 ppm). Although intramolecular H-bonding in similar complexes has been reported, e.g. in Pd(O₂CMe)₂(Et₂NH)₂ [13], this form of intraligand interaction is relatively unusual.

The Pd–P bonds (average ~2.260 Å) are generally shorter, and presumably stronger than those of their halo-derivatives, viz. PdCl₂(dppf) (2.274 Å) [3d] and PdBr₂(dppf) (2.310 Å). This strength is offset by the general weakness of the Pd–O bonds, which are significantly weaker than those in Pd₃(O₂CR)₆ (R = Me 1.992 Å [39], Et 1.995 Å [40], Bu 1.980 Å, C₉H₁₁ 2.00 Å [40]) This is consistent with the general instability

Table 2
Selected bond distances (Å) and angles (°)

R	I	III	IV	VIII	X CH ₂ Cl ₂
Pd–O	2.093(2)	2.096(4)	2.076(3)	2.058(5)	2.091(5)
	2.078(2)	2.105(4)	2.061(3)	2.102(4)	
Pd–Cl					2.361(2)
Pd–Br					
Pd–P	2.251(1)	2.262(1)	2.268(1)	2.275(2)	2.273(2) ^a
	2.271(1)	2.259(2)	2.252(1)	2.257(2)	2.257(2)
CO ₂ –O _{coord}	1.245(4)	1.273(7)	1.266(5)	1.295(9)	1.273(8)
O _{free}	1.204(4)	1.216(8)	1.207(6)	1.268(9)	1.235(8)
O···H [‡]				1.804	
CO ₂ –O _{coord}	1.270(4)	1.261(8)	1.268(6)	1.240(8)	
O _{free}	1.207(4)	1.218(8)	1.208(6)	1.229(9)	
O···H [‡]				1.765	
P–Pd–P	97.4(1)	97.47(5)	97.29(3)	98.64(7)	99.7(1)
O–Pd–O	86.6(1)	86.68(16)	86.51(11)	89.06(18)	
Br–Pd–Br					
O–Pd–Cl					87.3(1)
Cis–P–Pd–O	85.1(1)	84.53(12)	84.60(8)	84.34(13)	87.6(1)
	91.4(1)	91.20(12)	91.95(9)	88.07(14)	
Cis–P–Pd–Cl					85.5(1)
Cis–P–Pd–Br					
Trans–P–Pd–O	170.5(1)	170.75(12)	170.69(9)	173.08(5)	172.4(1)
	170.8(1)	176.87(12)	169.64(8)	175.51(14)	
Trans–P–Pd–Cl					174.0(1)
Trans–P–Pd–Br					
P···χ _A ···χ _B ···P	29.2	33.2	–29.2	–38.6	–30.7
χ _A ···Fe···χ _B	178.1	177.99	177.13	177.80	177.3

O···H[‡] is hydrogen bond where O is O_{free} of CO₂ unit coordinated to Pd and H is H of CO₂H unit of hydrogen maleate group. χ_A and χ_B are the centroid of the Cp rings of dppf.

^a (*) P *trans* to Cl

Table 3
Crystallographic data and refinement details

	I	III	IV	VIII	X CH ₂ Cl ₂
Empirical formula	C ₃₈ H ₂₈ F ₆ FeO ₄ P ₂ Pd	C ₄₂ H ₂₈ F ₁₄ FeO ₄ P ₂ Pd	C ₃₈ H ₃₀ Cl ₄ FeO ₄ P ₂ Pd	C ₄₂ H ₃₄ FeO ₈ P ₂ Pd	C ₄₂ H ₃₅ Cl ₃ FeO ₂ P ₂ Pd
Formula weight	886.8	1086.83	916.61	890.88	904.3
Crystal system		Monoclinic		Triclinic	
Space group		<i>P</i> 2 ₁ / <i>n</i> (Number 14)		<i>P</i> $\bar{1}$ (Number 2)	
<i>a</i> (Å)	12.9689(2)	13.8564(1)	12.9837(1)	9.3823(10)	9.368(2)
<i>b</i> (Å)	22.2859(4)	13.9834(2)	22.3205(3)	13.9488(15)	13.916(3)
<i>c</i> (Å)	13.1822(2)	22.0832(2)	13.5373(2)	15.0236(16)	16.027(3)
α (°)		90		97.182(2)	67.23(3)
β (°)	109.17(2)	94.091(1)	107.818(1)	98.098(2)	85.70(3)
γ (°)		90		97.345(2)	79.40(3)
<i>V</i> (Å ³)	3599(2)	4267.93(8)	3734.96(8)	1910.0(4)	1894(1)
<i>Z</i>		4		2	
ρ_{calc} (g cm ^{–3})	1.637	1.691	1.630	1.549	1.582
μ (mm ^{–1})	1.063	0.939	1.282	0.988	1.191
Temperature (K)	293(2)	203(2)	295(2)	223(2)	293(2)
Reflection collected	7287	21468	20481	11073	6955
Independent reflections	7082 [<i>R</i> _{int} = 0.0667]	7461 [<i>R</i> _{int} = 0.0253]	7546 [<i>R</i> _{int} = 0.0235]	6714 [<i>R</i> _{int} = 0.0630]	6658 [<i>R</i> _{int} = 0.0305]
Number of parameters	524	564	474	489	461
Goodness-of-fit on <i>F</i> ²	1.129	1.054	1.055	0.978	1.031
<i>R</i> ₁ and <i>wR</i> ₂ (observed data)	0.0362 and 0.0999	0.0532 and 0.1318	0.0376 and 0.0935	0.0628 and 0.1506	0.0648 and 0.1631

$R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$ $wR_2 = [\Sigma w [(F_0^2 - F_c^2)^2] / \Sigma w F_0^4]^{1/2}$. Goodness-of-fit on $F^2 = \{\Sigma [w(|F_0|^2 - |F_c|^2)^2] / (n - p)\}^{1/2}$.

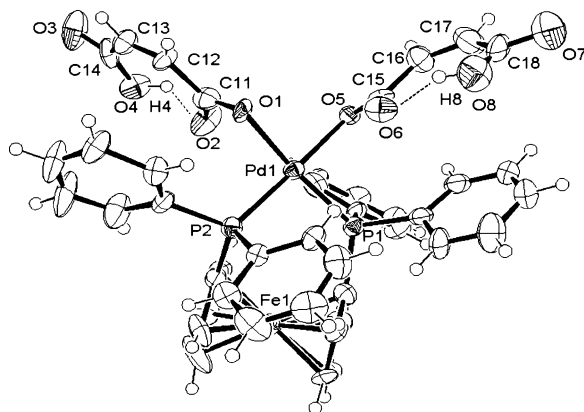


Fig. 1. ORTEP drawing (50% probability ellipsoids) of the molecular structure of $\text{Pd}(\text{O}_2\text{CCH}=\text{CHCO}_2\text{H})_2(\text{dppf})$ **VIII**.

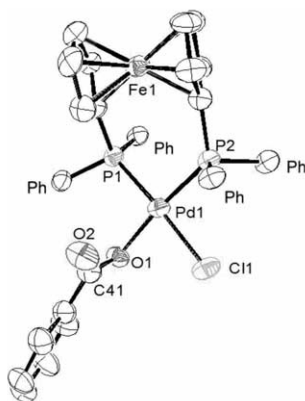


Fig. 2. ORTEP drawing of the molecular structure of $\text{PdCl}(\text{O}_2\text{CPh})(\text{dppf})$ in $\text{X CH}_2\text{Cl}_2$. The solvent molecule is omitted for clarity.

(and higher catalytic value) of Pd(II) phosphine carboxylates.

The chelating angles of dppf (average $\sim 97^\circ$) are similar to those in the Pt(II) analogues [36] and typical of dppf chelates. The $\angle \text{O}-\text{Pd}-\text{O}$ angles are fairly constant (ca. 86°) except in **VIII**, which is slightly expanded to accommodate the unusual interactions. Angular distortions are common, with most *cis*-P–Pd–O, O–Pd–O and P–Pd–P being far from ideal (90°), and *trans*-P–Pd–O also off from linear.

The dppf bite angle of 99.7° in **X** is larger than that of the bis(carboxylato) dppf complexes obtained but similar to $\text{PdCl}_2(\text{dppf})$ (99.07°) [41]. The Pd–Cl bond in **X** is lengthened upon coordination of the benzoate group [cf. $2.361(2)$ Å in **X** and $2.348(1)$ Å in $\text{PdCl}_2(\text{dppf})$ [41]]. On the contrary, the Pd–P bond in **X** is strengthened [Cf. $2.273(2)$ and $2.257(2)$ Å in **X** and 2.28 Å in $\text{PdCl}_2(\text{dppf})$ [41]]. Other angular distortions (from linearity) are also apparent; the $\angle \text{P}-\text{Pd}-\text{X}$ ($\text{X} = \text{Cl}, \text{O}$) decreases from $174.2(2)^\circ$ in $\text{PdCl}_2(\text{dppf})$ [41] to $174.0(1)$ and $172.4(1)^\circ$ in **X**. The benzoate group is coordinated in an unidentate fashion (C–O: $1.273(8)$ Å, C=O: $1.235(8)$ Å). Unlike **I**

which shows lengthening of C–O bond with its Pt analogue [36], the C–O bond length in **X** remains virtually identical to that of $\text{Pt}(\text{O}_2\text{CPh})_2(\text{dppf})$ [36]. The Pd–O bond of $2.091(5)$ Å is nearly identical to **I** [$2.093(2)$ and $2.078(2)$ Å] but smaller than **III** [$2.101(4)$ Å]. Comparing the Pd–O bonds clearly shows the influence of the size of the carboxylates. Larger carboxylates would give longer Pd–O bond because of their higher steric demands. In **X**, although benzoate is significantly larger than trifluoroacetate, the steric impact is not great because of the small neighboring Cl. The Pd–O length is hence only slightly weaker.

All of the complexes reported here have at least one dangling carboxylate groups. Their stability and basically qualify them as ligand for entry into mixed-metal carboxylates.

This idea was illustrated in our recent paper [1]. Results from elsewhere suggested that other derivatives of carboxylates like $\text{Pd}_2(\mu\text{-O}_2\text{CCH}_3\text{-O}, \text{O}')_2(\text{CH}_2\text{-C}_6\text{H}_4\text{-P}(o\text{-tolyl})_2\text{-C}, \text{P})_2$ [5] are highly active catalytically and mixed-metal carboxylates are highly reactive species [37]. These point to a rich potential for the current systems to be used as stable precursors to species that are catalytically reactive. Our preliminary studies show that complex **X** reacts with PhMgBr to give biphenyl and $\text{PdBr}_2(\text{dppf})$. While synthesis of biphenyl might not be synthetically important, such observation does suggest the possibility of an easy access of asymmetric diaryl compound from this system. Our immediate challenge is to explore the catalytic potential of these complexes, which is encouraged by our early findings that **I** and **II** are active in Heck-type syntheses.

3. Experimental

3.1. General procedures

All reactions were performed under pure dry argon using standard Schlenk techniques. All solvents and reagents were of reagent grade obtained from commercial sources and used without further purification. $\text{PdX}_2(\text{dppf})$ ($\text{X} = \text{Cl}, \text{Br}$) were prepared using literature method [41].

All ^1H and ^{31}P spectra were recorded at ca. 300 K at operating frequency of 299.96 and 121.49 MHz, respectively. ^1H and ^{31}P chemical shifts are quoted in ppm down-field of TMS, and external 85% H_3PO_4 , respectively. All IR spectra were recorded in its solid state on a Bio-Rad FTIR spectrometer using KBr disk. Elemental analyses were performed by the Elemental Analysis Laboratory of our Department. We experienced difficulties in obtaining satisfactory analytical data for several complexes. This could be attributed to their inherent instability and/or possible contamination by

trace quantity of $\text{Pd}(\text{O}_2\text{CR})_2(\text{dppf})\text{-AgO}_2\text{CR}$ or $\text{Pd}(\text{Cl})(\text{O}_2\text{CR})(\text{dppf})$ which cannot be removed.

3.1.1. $[\text{Pd}(\text{O}_2\text{CCF}_3)_2(\text{dppf})]$ **I**

$\text{PdBr}_2(\text{dppf})$ (0.169 g, 0.206 mmol) and AgO_2CCF_3 (0.0916 g, 0.415 mmol) in CH_2Cl_2 (50 cm^3) were stirred at room temperature (r.t.), shielded from direct sunlight for ca. 20 h. The resulting orange brown suspension was filtered through a column of celite, giving an orange–red filtrate. Complex **I** was obtained by diffusion of the filtrate through hexane (Yield 0.124 g, 68%). (Found: C, 50.9; H, 3.1%, $\text{C}_{42}\text{H}_{37}\text{F}_6\text{FeO}_4\text{P}_2\text{Pd}$ requires C, 51.5; H, 3.2%).

A similar reaction between $\text{PdCl}_2(\text{dppf})$ (0.133 g, 0.181 mmol) and AgO_2CCF_3 (0.087 g, 0.394 mmol) afforded **I** (Yield 0.085 g, 53%).

3.1.2. $[\text{Pd}(\text{O}_2\text{CCF}_2\text{CF}_2\text{CF}_3)_2(\text{dppf})]$ **III**

A similar reaction between $\text{PdCl}_2(\text{dppf})$ (0.100 g, 0.137 mmol) and $\text{AgO}_2\text{CCF}_2\text{CF}_2\text{CF}_3$ (0.097 g, 0.302 mmol) in CH_2Cl_2 (50 cm^3) for 6 h gave $\text{Pd}(\text{O}_2\text{CCF}_2\text{CF}_2\text{CF}_3)_2(\text{dppf})$ **III** (Yield 0.097 g, 59%), (Found: C, 43.4, H, 2.4%. $\text{C}_{42}\text{H}_{28}\text{FeP}_2\text{PdO}_4\text{F}_{14}\cdot 1.35\text{CH}_2\text{Cl}_2$ requires C, 43.3; H, 2.6%).

Similar reaction between $\text{PdBr}_2(\text{dppf})$ (0.200 g, 0.244 mmol) and $\text{AgO}_2\text{CCF}_2\text{CF}_2\text{CF}_3$ (0.172 g, 0.536 mmol) afforded **III** (Yield 0.140 g, 48%).

3.1.3. $[\text{Pd}(\text{O}_2\text{C-}o\text{-C}_6\text{H}_4\text{Cl})_2(\text{dppf})]$ **VI**

As similar reaction of $\text{PdBr}_2(\text{dppf})$ (0.200 g, 0.244 mmol) and $\text{AgO}_2\text{C-}o\text{-C}_6\text{H}_4\text{Cl}$ (0.065 g, 0.247 mmol) in CH_2Cl_2 (40 cm^3) for 20 h gave **VI** (Yield 0.185 g, 75%). The product is unstable in solution and gradually decomposed to generate oxidized dppf, (Found: C, 57.3; H, 3.3%, $\text{C}_{48}\text{H}_{36}\text{FeP}_2\text{O}_4\text{PdCl}_2\cdot 1/2\text{CH}_2\text{Cl}_2$ requires C, 57.4; H, 3.7%).

3.1.4. $[\text{Pd}(\text{O}_4\text{C}_2)(\text{dppf})]$ **IX**

As similar reaction of $\text{PdBr}_2(\text{dppf})$ (0.200 g, 0.244 mmol) and $\text{Ag}_2(\text{O}_4\text{C}_2)$ (0.0740 g, 0.244 mmol) in CH_2Cl_2 (50 cm^3) gave **IX** (Yield 0.083 g, 42%). (Found: C, 53.2; H, 4.3%. $\text{C}_{36}\text{H}_{28}\text{FeP}_2\text{O}_4\text{Pd}\cdot 3\ 1/2(\text{H}_2\text{O})$ requires C, 53.3; H, 4.4%).

3.1.5. $[\text{Pd}(\text{O}_2\text{CPh})_2(\text{dppf})]$ **V**

As similar reaction of AgO_2CPh (0.210 g, 0.917 mmol) and $\text{PdCl}_2(\text{dppf})$ (0.304 g, 0.415 mmol) in CH_2Cl_2 (50 cm^3). Extensive decomposition occurred when the reaction was carried out. After stirring for 2 h shielded from direct light, the mixture was then filtered through celite to remove the insoluble Ag particles but no stable isolable products of Pd was obtained. The residue was then scrupulously washed with Et_2O (4 \times 20 cm^3). After the washing was removed in vacuo, off-white residue was obtained. Sublimation of the off-white residue yielded benzoic acid, $\text{PdCl}_2(\text{dppf})$ was recovered

from the filtrate, When $\text{PdBr}_2(\text{dppf})$ was used in place of $\text{PdCl}_2(\text{dppf})$, and the Pd complex isolated was found to be $\text{PdCl}_2(\text{dppf})$.

In another method, hydrazine hydrate (ca. 5 cm^3) was added dropwise to a bright-red suspension of $\text{PdCl}_2(\text{dppf})$ (0.150 g, 0.205 mmol) and PPh_3 (0.220 g, 0.840 mmol) in EtOH (50 cm^3) at ca. 40 °C. An immediate color change to brown–yellow was observed. This suspension was allowed to stir at ca. 40 °C for about 45 min. The mixture was filtered leaving behind a yellow Pd(0) solid. The solid was washed copiously with ether (2 \times 25 cm^3) to remove the phosphine and phosphine oxide. Subsequent suspension of the reactive Pd(0) complex in EtOH (10 cm^3) and addition of PhCO_2H (0.125 g, 1.025 mmol) gave a red solution. After stirring at ca. 40 °C for 1 h, the red solution became orange and a yellow solid was observed. Upon cooling to –20 °C, a brown yellow solid was obtained. Complex **V** was collected after filtration and washed copiously with ether to remove phosphine, phosphine oxide and unreacted PhCO_2H (Yield 0.060 g, 32%). (Found: C, 62.6; H, 4.2%, $\text{C}_{48}\text{H}_{38}\text{O}_4\text{P}_2\text{FePd}$ requires C, 63.8; H, 4.2%).

3.1.6. $[\text{Pd}(\text{O}_2\text{CCHCl})_2(\text{dppf})]$ **IV**

$\text{PdCl}_2(\text{dppf})$ (0.100 g, 0.137 mmol), $\text{NaO}_2\text{CCHCl}_2$ (0.059 g, 0.393 mmol) and AgNO_3 (0.050 g, 0.294 mmol) in CH_2Cl_2 (40 cm^3) were mixed and stirred at r.t., shielded from direct light, for ca. 16 h. The orange–red suspension thus obtained was filtered through a column of celite. The filtrate was collected and concentrated to ca. 5 cm^3 . Hexane was added to crystallize the compound, $\text{Pd}(\text{O}_2\text{CCHCl})_2(\text{dppf})$ **IV** (Yield 0.106 g, 84%). (Found: C, 49.2; H, 2.5%, $\text{C}_{38}\text{H}_{30}\text{FeP}_2\text{PdO}_4\text{C}_{14}$ requires C, 49.8; H, 3.3%).

3.1.7. $[\text{Pd}(\text{O}_2\text{CCH}_2\text{CO}_2\text{H})_2(\text{dppf})]$ **VII**

A solution of $\text{Pd}(\text{OAc})_2$ (0.050 g, 0.230 mmol) in MeOH –ether (30 cm^3 ; 1:9) was added slowly to a solution of dppf (0.135 g, 0.243 mmol) in Et_2O (30 cm^3). A cloudy orange solution was obtained which turned brown upon stirring for ca. 5 min. Malonic acid (0.798 g, 7.673 mmol) was added to the mixture. A red microcrystalline solid was immediately deposited. The reaction mixture was then stirred for ca. 5 h. The reaction mixture was filtered and the red solid $\text{Pd}(\text{O}_2\text{CCH}_2\text{CO}_2\text{H})_2(\text{dppf})$ **VII** thus obtained was washed with Et_2O and recrystallized from CH_2Cl_2 –hexane (Yield 0.093 g, 45%). (Found: C, 53.5; H, 4.0%. $\text{C}_{40}\text{H}_{32}\text{FeP}_2\text{O}_8\text{Pd}\cdot 2\text{H}_2\text{O}$ requires C, 53.3; H, 4.0%).

3.1.8. $[\text{Pd}(\text{O}_2\text{CCH}=\text{CHCO}_2\text{H})_2(\text{dppf})]$ **VIII**

Similar to preparation of **VII**. Maleic acid (0.900 g, 7.759 mmol) was used instead of malonic acid. The reaction mixture was then allowed to stir overnight for

ca. 12 h. The reaction mixture was filtered and the red solid obtained was washed with ether and recrystallized from CH_2Cl_2 –hexane. During recrystallization, decomposition product(s) could be observed. After several attempts of recrystallization, some stable needle like red crystals of $\text{Pd}(\text{O}_2\text{CCH}=\text{CHCO}_2\text{H})_2(\text{dppf})$ **VIII** were obtained (Yield 0.067 g, 32%). The reaction yielded more than one products, from where **VIII**, which is stable, could be isolated. (Found: C, 55.6; H, 3.6%. $\text{C}_{42}\text{H}_{34}\text{FeP}_2\text{O}_8\text{Pd} \cdot 1/4\text{CH}_2\text{Cl}_2$ requires C, 55.6; H, 3.8%).

3.1.9. $[\text{PdCl}(\text{O}_2\text{CPh})(\text{dppf})] \text{X}$

Solid AgO_2CPh (0.111 g, 0.485 mmol) was added to a solution of $\text{PdCl}_2(\text{dppf})$ (0.304 g, 0.415 mmol) in CH_2Cl_2 (50 cm^3). The reaction mixture was stirred overnight (ca. 20 h), shielded from direct light. It was then filtered through celite to remove the insoluble Ag particles. An orange–red filtrate was obtained. The solvent was removed in vacuo. The orange–brown residue was extracted with CH_2Cl_2 followed again by filtration through celite. Hexane was then added to induce crystallization of **X** as an orange dichloromethane solvate, $\text{X} \cdot \text{CH}_2\text{Cl}_2$ (Yield, 0.150 g). (Found: C, 57.0; H, 4.1; P, 6.9; Fe, 6.5; Cl, 9.1; Pd, 12.3%. $\text{C}_{41}\text{H}_{33}\text{ClFeO}_2\text{P}_2\text{Pd}$ requires C, 56.0; H, 3.9; P: 6.9; Cl: 11.7; Fe, 6.2; Pd, 11.8%), δ_{H} (CDCl_3) 3.49, (2 H, s, C_5H_4); 4.20 (2 H, s, C_5H_4); 4.61 (2 H, s, C_5H_4); 5.24 (2 H, s, C_5H_4); 7.05–7.65 (4 H, m, Ph); 7.86–7.98 (22 H, m, Ph); 8.18–8.20 (4 H, m, Ph); δ_{P} (CDCl_3) 38.6 (1 P, *trans* to Cl, d, $^2J_{\text{P-P}} = 8$ Hz); 30.0 (1 P, *trans* to PhCO_2 , d, $^2J_{\text{P-P}} = 8$ Hz).

In another reaction, the green $[\text{Pd}_2(\mu\text{-Cl})(\eta^2\text{-dppf})_2][\text{BF}_4]_2$ (0.108 g, 0.069 mmol) was dissolved in MeCN (25 cm^3) to give a wine-red solution. NaO_2CPh (0.026 g, 0.180 mmol) in MeOH (15 cm^3) was added dropwise to the above solution. This reaction mixture was then stirred at r.t. for ca. 24 h. A brown solid in a red solution was observed. The reaction mixture was filtered. The solvent was completely removed in vacuo from the filtrate and the red residue extracted with CH_2Cl_2 . Partial removal of the solvent and addition of hexane gave a brown microcrystalline solid (Yield, 0.028 g). ^{31}P -NMR spectroscopy indicated the presence of **X** as the major component ($\sim 70\%$), with $\text{PdCl}_2(\text{dppf})$ and $\text{Pd}(\text{O}_2\text{CPh})_2(\text{dppf})$ as minor products ($\sim 15\%$ each).

3.1.10. $[\text{PdCl}(\text{O}_2\text{CCF}_3)(\text{dppf})] \text{XI}$

As similar reaction of $[\text{Pd}(\mu\text{-Cl})(\eta^2\text{-dppf})_2][\text{BF}_4]_2$ (0.112 g, 0.072 mmol) with NaO_2CCF_3 (0.035 g, 0.257 mmol) gave brown–red microcrystalline solid (Yield, 0.066g), comprising of $\text{PdCl}(\text{O}_2\text{CCF}_3)(\text{dppf})$ (70%), $\text{PdCl}_2(\text{dppf})$ (15%) and $\text{Pd}(\text{O}_2\text{CCF}_3)_2(\text{dppf})$ (15%). δ_{H} (CDCl_3); 3.51, (2 H, s, C_5H_4); 4.24 (2 H, s, C_5H_4); 4.64 (2 H, s, C_5H_4); 5.15 (2 H, s, C_5H_4); 7.22–7.38 (2 H, m, Ph); 7.41–7.63 (12 H, m, Ph); 7.79–7.89 (2 H, m, Ph); 8.09–8.15 (4 H, m, Ph); δ_{P} (CDCl_3) 33.8 (1 P, *trans* to

Cl, d, $^2J_{\text{P-P}} = 13$ Hz); 38.9 (1 P, *trans* to CF_3CO_2 , d, $^2J_{\text{P-P}} = 13$ Hz).

3.2. Crystal structure determinations

The diffraction experiments for complexes **III**, **IV**, **VIII** were carried out on a Bruker SMART CCD diffractometer with a Mo– K_α sealed tube. The program SMART [44] was used for collecting frames of data, indexing reflections and determination of lattice parameters, SAINT [44] for integration of the intensity of reflections and scaling, SADABS [45] for absorption correction and SHELXTL [46] for space group and structure determination and least-squares refinements on F^2 . For **III**, the F atoms on the two CF_3 groups were disordered. Soft constraints were applied using SADT command. Common isotropic thermal parameters were defined for each model. The occupancies are 0.7/0.3 and 0.6/0.4, For **IV**, the Cl atoms on one of the CHCl_2 fragment were severely disordered. Four different disorder models were resolved with occupancies 0.4/0.2/0.2/0.2. The thermal parameters for the major model were refined anisotropically and common thermal parameters were refined for the rest.

Intensity data of complex **I** were collected on a Rigaku RAXIS-IIC [47] imaging plate diffractometer system powered at 50 KV and 90 mA with graphite-monochromatized Mo– K_α radiation ($\lambda = 0.71073$ Å). Intensity data of $\text{X} \cdot \text{CH}_2\text{Cl}_2$ were measured on a Rigaku AFC7R diffractometer using Mo– K_α radiation in the range $2\theta = 4.0$ – 50.0° with ω scan at 8.0 – $32.00^\circ \text{ min}^{-1}$. Two standard reflections were monitored after every 125 data measurements, showing only small random variations. The raw data were processed with the learnt-profile procedure [48], and absorption corrections were applied by fitting a pseudo-ellipsoid to the ψ -scan data of selected strong reflections over a range of 2θ angles [49]. Both structures were solved by direct methods, and the CF_3 groups in **I** were found to exhibit two-fold orientation disorder. All other non-hydrogen atoms were subjected to anisotropic refinement. Hydrogen atoms of the organic ligands were generated geometrically ($\text{C-H} = 0.95$ Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All computations were performed with the SHELXTL-PC program package [50]. Analytical expressions of neutral-atom scattering factors were employed, and anomalous-dispersion corrections were incorporated [51].

Intensity data of Complex **X** were measured on a Rigaku AFC7R diffractometer using highly oriented graphite crystals at $2\theta = 4.0$ – 50.0° with ω scan at 8.0 – $32.00^\circ \text{ min}^{-1}$. Mo– K_α monochromatic radiation was used. Intensity data of complex **I** are carried out on a Rigaku RAXIS-IIC [47] imaging plate diffractometer system powered at 50 KV and 90 mA with graphite-

monochromatized Mo–K α radiation ($\lambda = 0.71073 \text{ \AA}$) using variable ω -scan technique.

Two standard reflections were monitored after every 125 data measurements, showing only small random variations. The raw data were processed with the learnt-profile procedure [48], and absorption corrections were applied by fitting a pseudo-ellipsoid to the ψ -scan data of selected strong reflections over a range of 2θ angles [49]. The structures were solved with the Patterson superposition method with the aid of subsequent difference Fourier syntheses. The CF₃ groups in the **I** are disordered. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were generated geometrically (C–H = 0.95 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. The phenyl groups on the phosphine were treated as rigid groups. The other non-hydrogen atoms were refined anisotropically, and the hydrogen atoms of the cyclopentadienyl groups were included in the structure-factor calculations with assigned isotropic temperature factors. All computations were performed with the SHELXTL-PC program package [50]. Analytical expressions of neutral-atom scattering factors were employed, and anomalous-dispersion corrections were incorporated [51].

The relevant crystallographic data and refinement details of all complexes are shown in Table 3.

4. Supplementary materials

The ORTEP plots of complex **I**, **III**, **IV** and PdBr₂(dppf) are available as supplementary materials. Crystallographic data (CIF files) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 169371–169376 for the six structures [**I**, **III**, **IV**, **VIII**, **X** and PdBr₂(dppf)]. 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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