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Cyclometallated compounds of Pd(II): C=N to C=O conversion through acid hydrolysis. Crystal and molecular structures of [Pd{4-(CHO)C_6H_3C(H)=NCy}(Cl)$(PPh_3)_2$] and [Pd{2,4-$(CHO)_2C_6H_3$}(Cl)$(PPh_3)_2$]

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Abstract

Treatment of the chloro-bridged complex [Pd{4-(CHO)C_6H_3C(H)=NCy}(Cl)$]_2$ (**1**) with *tertiary* monophosphines in a 1:4 molar ratio gave the non-cyclometallated monomer complexes [Pd{4-(CHO)C_6H_3C(H)=NCy}(Cl)$(PR_3)_2$] (PR_3: (**2**) PPh_3, (**3**) $PEtPh_2$, (**4**) PEt_2Ph, (**5**) $PMePh_2$). The crystal structure of **2** is described. Reaction of complexes **2**–**5** with a mixture of glacial acetic acid–water gave the monomeric complexes [Pd{2,4-$(CHO)_2C_6H_3$}(Cl)$(PR_3)_2$] (PR_3 (**6**), PPh_3 (**7**), $PEtPh_2$ (**8**), PEt_2Ph (**9**), $PMePh_2$) after cleavage of the C=N group. Complex **6** was characterized crystallographically. Treatment of **1** with the triphosphine bis(2-diphenylphosphinoethyl)phenylphosphine in 1:2 molar ratio gave the mononuclear complex [Pd{4-(CHO)C_6H_3C(H)=NCy}{$Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$-*P*,*P*,*P*}][Cl] (**10**) in which the phosphine is coordinated through the three phosphorus atoms. Treatment of **10** with a mixture of acetic acid–water also caused cleavage of the C=N bond giving the complex [Pd{2,4-$(CHO)_2C_6H_3$}{$Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$-*P*,*P*,*P*}][Cl] (**11**).

Keywords: Cyclometallation; Palladium(II); Tertiary phosphines

1. Introduction

Cyclometallated compounds involve σM–C bond formation and additional coordination of the metal atom to a suitable ligand donor atom. The donor atom, as well as the metal and chelate ring size, serve as a basis for their classification; by far the most well-studied examples are the five-membered palladacycles containing Pd–N and C(phenyl)–Pd bonds [1–5]. Currently they show a wide range of applications in organic and organometallic chemistry [6–8].

Previously, we have prepared cyclometallated complexes with an uncoordinated formyl group. The synthesis of such compounds was performed by reaction of palladium(II) acetate and the appropriate Schiff base ligand 1,4-$(CyN{=}CH)_2C_6H_4$ and 1,3-$(CyN{=}CH)_2C_6H_4$ in glacial acetic acid [9,10]. The acidic nature of the solvent caused selective cleavage of one of the C=N double bonds pertaining to the uncoordinated C=N group. The second C=N moiety seems to be protected against hydrolysis due to intramolecular coordination to the palladium atom. Bearing this in mind we reasoned that opening of the cyclometallated ring should make the imine group susceptible to hydrolysis. Thus, in the present paper, we report the reaction of the chloro-bridged cyclometallated complex **1** with *tertiary* monophosphines to give non-cyclometallated species after Pd–N bond cleavage, supporting uncoordinated C=N and C=O groups. The crystal structure of one such compound is described. Subsequent treatment with a mixture of acetic acid–water produced cleavage of the second imine group of the organic ligand yielding a compound with two free formyl moieties: the equivalent

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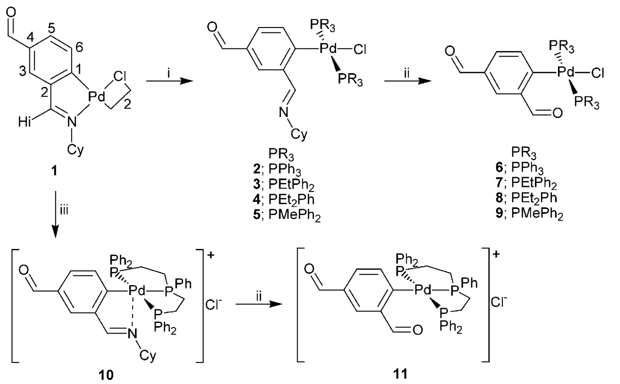
of metallating the organic aldehyde. We also report, the structure of one of these complexes, which to the best of our knowledge is the first example of its kind to be crystallographically characterized.

2. Results and discussion

The compounds and reactions are shown in Scheme 1. The compounds described in this paper were characterized by elemental analysis (C, H, N) and by IR, ^{1}H- and ^{31}P{^{1}H}- spectroscopy (data in the Section 3).

The reaction of the chloro-bridged complex **1** [11] with *tertiary* monophosphines in a 1:4 molar ratio gave the non-cyclometallated monomer complexes [Pd{4-(CHO)$C_6H_3C(H)$=NCy}(Cl)$(PR_3)_2$] (PR_3: (**2**) PPh_3, (**3**) $PEtPh_2$, (**4**) PEt_2Ph, (**5**) $PMePh_2$), which were fully characterized (see Section 3). The IR spectra of the complexes showed the band assigned to the free formyl group ca. 1685 cm^{-1}, and the band corresponding to the ν(C=N) and ν(Pd–Cl) stretches ca. 1630 and 295 cm^{-1}, respectively. The latter was consistent with a *trans*-Cl–Pd–C geometry [12]. The ^{1}H-NMR spectra showed singlet resonances ca. δ 9.75 and 8.20, assigned to the HC=O and HC=N protons, respectively. Neither the H^6 nor the HC=N protons showed coupling to the ^{31}P-nucleus of the phosphine due to the opening of the cyclometallated ring [10,13]. In the absence of Pd–N bond, the metallated phenyl ring can rotate about the Pd–C vector so that its plane is at 90° to the palladium coordination plane and coupling of the H^6 proton to the ^{31}P-nucleus is absent [10,13]. The ^{31}P{^{1}H}-NMR spectra showed a singlet resonance confirming the *trans* geometry of the phosphine ligands.

Whereas cyclometallation precludes cleavage of the C=N group bonded to palladium, as in compound **1**, scission of the Pd–N bond, upon reaction with phosphines, allows further hydrolysis of the second C=N double bond to give an additional non-coordinated formyl group on the metallated ring. Thus, reaction of complexes **2**–**5** with a mixture of glacial acetic acid and water gave the mononuclear species [Pd{2,4-$(CHO)_2C_6H_3$}(Cl)$(PR_3)_2$] (PR_3: (**6**) PPh_3, (**7**) $PEtPh_2$, (**8**) PEt_2Ph, (**9**) $PMePh_2$), respectively, which were fully characterized. The IR spectra showed the absence of the ν(C=N) band and, in the case of complexes **6** and **7**, two bands corresponding to the free formyl groups (in the spectra of **8** and **9** the bands overlapped). The IR spectra also showed the ν(Pd–Cl) stretch precluding the substitution of the chloro ligand by an acetate ligand from acetic acid. Cleavage of the imine group was confirmed by the absence of the HC=N resonance in the ^{1}H-NMR spectra and by the presence of two singlet signals in the range δ 10.04–9.62 corresponding to the HC=O moieties. The *trans* disposition of the phosphine ligands was confirmed by the presence of one only singlet resonance in the ^{31}P{^{1}H} spectra.



Scheme 1. (i) PR_3 (acetone 1:4 molar ratio); (ii) acetic acid–water; (iii) triphos (acetone 1:2 molar ratio).

Reaction of **1** with the triphosphine bis(2-diphenylphosphinoethyl)phenylphosphine in 1:2 molar ratio gave the mononuclear complex [Pd{4-(CHO)-$C_6H_3C(H)$=NCy}{$Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$-*P*,*P*,*P*}][Cl] (**10**), The phosphorus resonances in the ^{31}P{^{1}H}-NMR spectrum were downfield shifted from their values in the free phosphine suggesting coordination of the three phosphorus atoms to the metal center. A broad resonance at δ 81.8 was assigned to the central ^{31}P-nucleus, *trans* to the phenyl carbon atom, and the signal at δ 38.7 was assigned to the two equivalent mutually *trans* phosphorus nuclei. The latter signal appeared at lower frequency in accordance with the higher *trans* influence of the phosphine ligand [12]. The H^6 resonance appeared as a triplet showing coupling only to the central phosphorus atom [*J*(PH) 7.8 Hz] and to H^5. These data are in accordance with a disposition in which the metallated ring is nearly perpendicular to the plane defined by the three phosphorus atoms [14,15]. The shift of the ν(C=N) stretching vibration to lower wavenumbers (as compared with the non-coordinated ligand) [16,17] as well as the upfield shift of the HC=N proton resonance in the ^{1}H-NMR spectra [18] indicated the existence of palladium–nitrogen interaction in solution. These results strongly agree with those previously obtained by us in related penta-coordinated palladium(II) species, and hence we propose a similar disposition of the triphos ligand in this case [14,15].

Nevertheless, the Pd–N bond interaction in compound **10** is not sufficiently strong to hinder cleavage of the C=N group, as in **1**, upon treatment with acetic acid media. Therefore, reaction of **10** with a mixture of acetic acid–water gave [Pd{2,4-$(CHO)_2C_6H_3$}{$Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$-*P*,*P*,*P*}][Cl] (**11**), after cleavage of the C=N bond. The IR spectrum of **11** showed two strong bands at 1689 and 1666 cm^{-1} assigned to the two formyl groups and the absence of the ν(C=N) stretch. The ^{1}H- and ^{31}P{^{1}H}-NMR spectra of the complex showed similar characteristics to the one of **10**, with the most noticeable differences corresponding to the absence of the HC=N signal and to the appearance of two HC=O resonances.

2.1. *Crystal structures of [Pd{4-(CHO)C_6H_3C(H)=NCy}(Cl)($(PPh_3)_2$)] (**2**) and [Pd{2,4-$(CHO)_2C_6H_3$}(Cl)($(PPh_3)_2$)] (**6**)*

Suitable crystals were grown by slowly evaporating chloroform–*n*-hexane solutions of the complexes. The molecular structures are illustrated in Figs. 1 and 2. Crystal data are given in Table 1 and selected bond distances and angles with estimated standard deviations are shown in Table 2.

The crystal structures consist of discrete molecules separated by van der Waals distances. The asymmetric unit of **6** comprises two molecules with similar structures, of which only one will be discussed, and two chloroform solvent molecules.

In both compounds, the four coordinated palladium atom is bonded to the phenyl carbon atom of the metallated phenyl ring, one chloro ligand and to two phosphorus atoms of the mutually *trans*-triphenylphosphine ligands. The coordination sphere of the palladium may be described as slightly distorted square-planar. The angles between adjacent atoms in the coordination sphere of palladium are close to the expected value of 90°, in the range 91.9(3)–88.3(1)° and 88.5(2)–91.24(6)° for complexes **2** and **6**, respectively.

The Pd(1)–C(1) bond distances [2.021(11), **2**; and 1.994(5), **6**] are somewhat shorter than the values predicted from the sum of their covalent radii [19], but similar to values reported earlier suggesting some degree of multiple bonding [20–23]. The Pd–P and Pd–Cl bond distances are also within the expected values [20–23]. The geometry about the palladium atoms is planar [mean deviations form the Pd(1), C(1), P(1), P(2), Cl(1) plane of 0.0211 and 0.0221 Å, for complexes **2** and **6**, respectively]. The metallated ring forms an angle of ca. 90° with the palladium coordination plane (100.2 and 90.7° for **2** and **6**, respectively), confirming the ^{1}H-NMR data (vide supra). In complex **6**, the two formyl groups and the metallated phenyl ring are nearly coplanar (see Fig. 3), whereas in complex **2** the metallated ring and the HC=O group are also coplanar but the HC=N moiety is slightly out of the plane, probably due to the steric interaction between the phosphine phenyl groups and the cyclohexyl moiety.

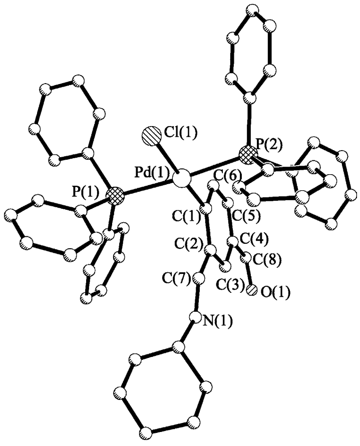


Fig. 1. Molecular structure of [Pd{4-(CHO)C_6H_3C(H)=NCy}(Cl)($(PPh_3)_2$)] (**2**), with labeling scheme. Hydrogen atoms have been omitted for clarity.

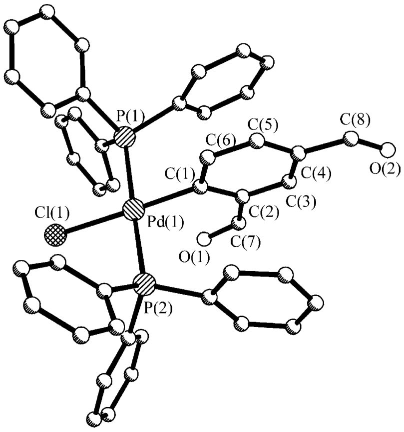


Fig. 2. Molecular structure of [Pd{2,4-$(CHO)_2C_6H_3$}(Cl)($(PPh_3)_2$)] (**6**), with labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 1
Crystallographic data for complexes **2** and **6**

	2	**6**
Chemical formula	$C_{50}H_{46}ClNOPd_2Pd$	$C_{45}H_{36}Cl_4O_2P_2Pd$
Formula weight	880.67	918.88
T (°C)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
a (Å)	13.839(4)	21.341(1)
b (Å)	23.239(8)	19.044(1)
c (Å)	31.95(1)	21.911(1)
β (°)		110.127(1)
V (Å^3)	8791(5)	8361.2(2)
Z	8	8
μ (mm^{-1})	0.593	0.813
Collected reflections	34 168	47 210
Unique reflections	6899 ($R_{int} = 0.029$)	14 701 ($R_{int} = 0.061$)
R_1 [a]	0.0942	0.0559
wR_2 [b]	0.2951	0.1652

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $[F > 4\sigma(F)]$.

[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma\, w(F_o^2)^2]^{1/2}$, all data.

No interaction was observed between the imine nitrogen and the palladium atom in **2**. Such contact has been reported previously in other non cyclometallated complexes of palladium(II) with phosphine ligands

Table 2
Selected bond lengths (Å) and angles (°) for complexes **2** and **6**

2		**6**			
Bond lengths					
Pd(1)–C(1)	2.02(1)	Pd(1)–C(1)	1.994(1)	Pd(2)–C(51)	1.992(6)
Pd(1)–Cl(1)	2.358(3)	Pd(1)–Cl(1)	2.387(2)	Pd(2)–Cl(2)	2.388(2)
Pd(1)–P(1)	2.333(4)	Pd(1)–P(1)	2.328(2)	Pd(2)–P(3)	2.333(2)
Pd(1)–P(2)	2.316(3)	Pd(1)–P(2)	2.342(2)	Pd(2)–P(4)	2.334(2)
C(2)–C(7)	1.42(2)	C(2)–C(7)	1.466(9)	C(52)–C(57)	1.468(8)
C(7)–N(1)	1.28(2)	C(7)–O(1)	1.208(8)	C(57)–O(3)	1.216(7)
Bond angles					
C(1)–Pd(1)–P(2)	90.7(3)	C(1)–Pd(1)–P(2)	89.4(2)	C(51)–Pd(2)–P(4)	89.5(2)
C(1)–Pd(1)–P(1)	91.9(3)	C(1)–Pd(1)–P(1)	88.5(2)	C(51)–Pd(2)–P(3)	88.8(2)
P(2)–Pd(1)–P(1)	175.8(1)	P(2)–Pd(1)–P(1)	176.44(6)	P(4)–Pd(2)–P(3)	173.64(6)
C(1)–Pd(1)–Cl(1)	176.4(3)	C(1)–Pd(1)–Cl(1)	178.7(2)	C(51)–Pd(2)–Cl(2)	178.2(2)
P(1)–Pd(1)–Cl(1)	88.3(6)	P(1)–Pd(1)–Cl(1)	90.73(6)	P(3)–Pd(2)–Cl(2)	90.18(6)
P(2)–Pd(1)–Cl(1)	88.9(1)	P(2)–Pd(1)–Cl(1)	91.24(6)	P(4)–Pd(2)–Cl(2)	91.27(6)

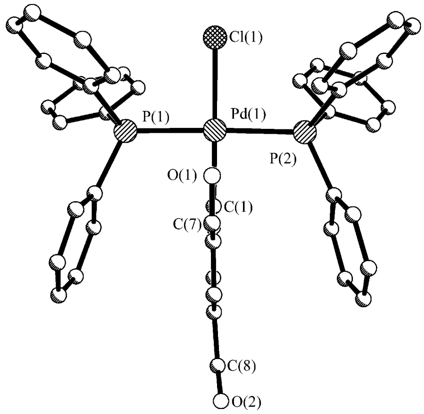


Fig. 3. Planar disposition of the metallated phenyl and the two formyl groups.

[20,24]. We believe this could be due to the steric hindrance that pushes the cyclohexyl ring away from the neighboring phosphine phenyl rings, thus restricting approximation of the nitrogen lone pair to the palladium atom.

In the molecular structure of **6** the C(2)–C(H)=O oxygen is directed toward the palladium atom, however, the Pd(1)–O(1) distance of 2.930 Å precluded any interaction between both atoms.

3. Experimental

3.1. General procedures

The synthesis of complexes **1**, **2** and **5** has been reported previously [8]. Solvents were purified by standard methods [25]. Chemicals were reagent grade. The phosphines PPh_3, $PEtPh_2$, PEt_2Ph and $PMePh_2$ were purchased from Aldrich-Chemie. Microanalyses were carried out using a Carlo Erba Elemental Analyzer, Model 1108. IR spectra were recorded as Nujol mulls or KBr discs on a Perkin–Elmer 1330 and on a Mattson spectrophotometers. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^{1}H, $^{13}C\{^{1}H\}$) or 85% H_3PO_4 ($^{31}P\{^{1}H\}$) and were recorded on Bruker WM-250, AMX-300 and AMX-500 spectrometers. All chemical shifts were reported downfield from standards.

3.2. Preparation of $[Pd\{4\text{-}(CHO)C_6H_3C(H)=NCy\}(Cl)(PPh_3)_2]$ (**2**)

PPh_3 (74.0 mg, 0.280 mmol) was added to a solution of **1** (50.0 mg, 0.070 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h at room temperature (r.t.) and the resulting white precipitate was filtered off and recrystallized from dichloromethane–hexane. Yield 89%. Anal. Found: C, 69.2; H, 5.9; N, 1.6. $C_{50}H_{46}NOPdP_2Cl$ requires C, 68.7; H, 5.4; N, 1.6%. IR: $\nu(C=O)$, 1685s cm^{-1}; $\nu(C=N)$, 1625s cm^{-1}; $\nu(Pd–Cl)$, 290m cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ ppm, J Hz): 9.76 [s, 1H, HC=O], 8.26 [s, 1H, HC=N], 7.69[d, 1H, H^3, $J(H^3H^5) = 1.9$], 6.98 [dd, 1H, H^5, $J(H^5H^6) = 8.0$], 6.62 [d, 1H, H^6]. $^{31}P\{^{1}H\}$-NMR ($CDCl_3$, δ ppm) 22.6s.

Compounds **3**, **4** and **5** were prepared similarly as yellow solids.

3.3. $[Pd\{4\text{-}(CHO)C_6H_3C(H)=NCy\}(Cl)(PEtPh_2)_2]$ (**3**)

Yield: 73%. Anal. Found: C, 64.5; H, 5.4; N, 1.5. $C_{42}H_{46}NOPdP_2Cl$ requires C, 64.3; H, 5.9; N, 1.8%. IR: $\nu(C=O)$, 1688s cm^{-1}; $\nu(C=N)$, 1635s cm^{-1}; $\nu(Pd–Cl)$, 293m cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ ppm, J Hz): 9.74 [s, 1H, HC=O], 8.25 [s, 1H, HC=N], 7.69 [d, 1H, H^3, $J(H^3H^5) = 1.9$], 7.02 [dd, 1H, H^5, $J(H^5H^6) = 8.0$], 6.73 [d, 1H, H^6]. $^{31}P\{^{1}H\}$-NMR ($CDCl_3$, δ ppm) 32.9s.

3.4. *[Pd{4-(CHO)C_6H_3C(H)=NCy}(Cl)(PEt_2Ph)$_2$] (**4**)*

Yield: 45%. Anal. Found: C, 50.7; H, 5.9; N, 1.7. $C_{34}H_{42}NOPdP_2Cl \cdot 2CH_2Cl_2$ requires C, 50.4; H, 5.9; N, 1.6%. IR: ν(C=O), 1689s cm^{-1}; ν(C=N), 1632s cm^{-1}; ν(Pd–Cl), 297m cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ ppm, *J* Hz): 9.77 [s, 1H, HC=O], 8.18 [s, 1H, HC=N], 7.70[d, 1H, H^3, $J(H^3H^5) = 1.9$], 7.13 [dd, 1H, H^5, $J(H^5H^6) = 8.1$], 6.63 [d, 1H, H^6]. $^{31}P\{^1H\}$-NMR ($CDCl_3$, δ ppm) 32.4s.

3.5. *[Pd{4-(CHO)C_6H_3C(H)=NCy}(Cl)($PMePh_2$)$_2$] (**5**)*

Yield: 70%. Anal. Found: C, 58.3; H, 5.7; N, 1.4. $C_{40}H_{42}NOPdP_2Cl \cdot CH_2Cl_2$ requires C, 58.5; H, 5.3; N, 1.7%. IR: ν(C=O), 1687s cm^{-1}; ν(C=N), 1635s cm^{-1}; ν(Pd–Cl), 293m cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ ppm, *J* Hz): 9.70 [s, 1H, HC=O], 8.42 [s, 1H, HC = N], 7.05 [dd, 1H, H^5, $J(H^5H^6) = 8.0$, $J(H^5H^3) = 1.6$], 6.94 [d, 1H, H^6]; the H^3 signal was occluded by the phosphine phenyl resonances. $^{31}P\{^1H\}$-NMR ($CDCl_3$, δ ppm) 28.9s.

3.6. *Preparation of [Pd{2,4-(CHO)$_2C_6H_3$}(Cl)(PPh_3)$_2$] (**6**)*

H_2O (2 cm^3) was added to a solution of **2** (50.0 mg, 0.056 mmol) in glacial acetic acid (15 cm^3). The mixture was stirred for 48 h at r.t. The acetic acid was then removed under vacuum, water added to the residue and the product extracted with dichloromethane. The combined extracts were dried over anhydrous sodium sulfate, filtered and the solvent removed under vacuum to give a pale yellow solid which was recrystallized from dichloromethane–hexane. Yield: 70%. Anal. Found: C, 66.3; H, 4.9. $C_{44}H_{35}O_2PdP_2Cl$ requires C, 66.1; H, 4.4. IR: ν(C=O), 1732w, 1681s cm^{-1}; ν(Pd–Cl), 296s cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ ppm, *J* Hz): 9.86, 9.63 [s, 2H, HC=O], 7.05 [dd, 1H, H^5, $J(H^5H^6) = 7.9$, $J(H^3H^5) = 1.9$], 7.08[d, 1H, H^6]. $^{31}P\{^1H\}$-NMR ($CDCl_3$, δ ppm) 22.0s.

Compounds **7**–**9** were synthesized following a similar procedure as orange (**7** and **9**) and yellow (**8**) solids.

3.7. *[Pd{2,4-(CHO)$_2C_6H_3$}(Cl)($PEtPh_2$)$_2$] (**7**)*

Yield: 67%. Anal. Found: C, 60.9; H, 4.6. $C_{36}H_{35}O_2PdP_2Cl$ requires C, 61.5; H, 5.0. IR: ν(C=O), 1691s, 1710sh, m cm^{-1}; ν(Pd–Cl), 285s cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ ppm, *J* Hz): 9.96, 9.62 [s, 2H, HC=O]. $^{31}P\{^1H\}$-NMR ($CDCl_3$, δ ppm) 34.7s.

3.8. *[Pd{2,4-(CHO)$_2C_6H_3$}(Cl)(PEt_2Ph)$_2$] (**8**)*

Yield: 45%. Anal. Found: C, 56.1; H, 5.5. $C_{28}H_{35}O_2PdP_2Cl$ requires C, 61.5; H, 5.0. IR: ν(C=O), 1685s s cm^{-1}; ν(Pd–Cl), 292m cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ ppm, *J* Hz): 10.4, 9.78 [s, 2H, HC=O]. $^{31}P\{^1H\}$-NMR ($CDCl_3$, δ ppm) 32.5s.

3.9. *[Pd{2,4-(CHO)$_2C_6H_3$}(Cl)($PMePh_2$)$_2$] (**9**)*

Yield: 88%. Anal. Found: C, 59.6; H, 5.0. $C_{34}H_{31}O_2PdP_2Cl$ requires C, 60.5; H, 4.7. IR: ν(C=O), 1683s s cm^{-1}; ν(Pd–Cl), 297m cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ ppm, *J* Hz): 10.0, 9.66 [s, 2H, HC=O]. $^{31}P\{^1H\}$-NMR ($CDCl_3$, δ ppm) 29.0s.

Compound **10** was prepared as a yellow solid, following a procedure similar to the one employed in the synthesis of **2** but using a cyclometallated compound **1**–triphosphine 1:2 molar ratio.

3.10. *[Pd{4-(CHO)C_6H_3C(H)=NCy}{$Ph_2P(CH_2)_2$-$PPh(CH_2)_2PPh_2$-P,P,P}][Cl] (**10**)*

Yield: 95%. Anal. Found: C, 62.0; H, 5.8; N, 1.8. $C_{48}H_{49}ClNOP_3Pd \cdot 0.5CH_2Cl_2$ requires C, 62.4; H, 5.4; N, 1.5%. IR: ν(C=O) 1689s, ν(C=N) 1625m cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ ppm, *J* Hz): 9.77 [s, 1H, HC=O], 8.19 [s, 1H, HC=N], 6.81 [d, 1H, H^5, $J(H^5H^6) = 7.3$], 6.07 [t, 1H, H^6, $J(H^6P) = 7.3$]. $^{31}P\{^1H\}$-NMR ($CDCl_3$, δ ppm) 81.8br, 38.7br.

Compound **11** was synthesized following a similar procedure to that for **6** but using a cyclometallated complex **1**–triphosphine 1:2 molar ratio.

3.11. *[Pd{2,4-(CHO)$_2C_6H_3$}{$Ph_2P(CH_2)_2$-$PPh(CH_2)_2PPh_2$-P,P,P}][Cl] (**11**)*

Yield: 63%. Anal. Found: C, 62.1; H, 5.0. $C_{42}H_{38}ClO_2P_3Pd$ requires C, 62.3; H, 4.7. IR: ν(C=O) 1689s, 1666s cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ ppm, *J* Hz): 9.83, 9.66 [s, 2H, HC=O], 7.91 [s, 1H, H^3], 6.96 [d, 1H, H^5, $J(H^5H^6) = 7.0$], 6.54 [t, 1H, H^6, $J(H^6P) = 7.0$]. $^{31}P\{^1H\}$-NMR ($CDCl_3$, δ ppm) 93.7br, 44.5br.

3.12. *X-ray crystallographic data*

Three-dimensional, r.t. X-ray data were collected on a Bruker Smart CCD diffractometer by the ω-scan method using graphite-monochromated Mo–K$_\alpha$ radiation. All the measured reflections were corrected for Lorentz and polarization effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0942$ and 0.0559 (for complexes **2** and **6**, respectively, observed data, *F*) and $wR_2 = 0.2951$ and 0.1652 (for complexes **2** and **6**, respectively, unique data, F^2), with allowance for thermal anisotropy of all non-hydrogen atoms. The structure solution and refinement were carried out using the program package SHELX-97 [26].

4. Supplementary data

Full details of data collection and structure refinement have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 184328 (**2**) and 184329 (**6**). 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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[11] We have previously reported the synthesis of compounds **1**, **2** and **5**. Compound **1** is brought here as the starting material for the remaining complexes, and compounds **2** and **5** are included to complete the reaction scheme, which leads to the new species **6** and **9**, respectively. Furthermore, the crystal structure of **2**, which was unknown, is now reported.

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