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Functionalized palladium(II) cyclometallated complexes. Crystal and molecular structures of $[Pd\{3\text{-}(CHO)C_6H_3C(H){=}NCy\}(\mu\text{-}O_2CMe)]_2$ and $[Pd\{3\text{-}(CHO)C_6H_3C(H){=}NCy\}(Cl)(PR_3)]$ ($PR_3 = PEtPh_2$, and PEt_2Ph)

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Abstract

The crystal structure of the cyclometallated acetato-bridged complex $[Pd\{3\text{-}(CHO)C_6H_3C(H){=}NCy\}(\mu\text{-}O_2CMe)]_2$, **1** is reported. Each palladium atom is *C*, *N*-bonded to the chelating Schiff base ligand. The molecular configuration corresponds to the *anti* isomer, with the cyclopalladated moieties in an 'open-book' disposition. Treatment of **1** with aqueous sodium chloride gave the chloro-bridged compound **2**, which when treated with tertiary phosphines yielded complexes **3** and **4**. The crystal structures of complexes $[Pd\{3\text{-}(CHO)C_6H_3C(H){=}NCy\}(Cl)(PR_3)]$ ($PR_3 = PEtPh_2$, **3** and PEt_2Ph, **4**) are also reported. In both complexes the palladium atom is bonded in a slightly distorted square-planar coordination to a carbon and a nitrogen atom of the Schiff base, a chlorine atom and to the phosphorus atom of the phosphine ligand. The reaction of the chloro-bridged complex **2** with the tertiary diphosphines $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2P(CH_2)_2PPh_2$ (dppe) in a 1:2 molar ratio, and ammonium hexafluorophosphate, yielded the mononuclear cyclometallated complexes $[Pd\{3\text{-}(CHO)C_6H_3C(H){=}NCy\}\{Ph_2PCH_2PPh_2\text{-}P,P\}][PF_6]$, **5** and $[Pd\{3\text{-}(CHO)C_6H_3C(H){=}N{-}Cy\}\{Ph_2P(CH_2)_2PPh_2\text{-}P,P\}][PF_6]$, **6**, respectively.

Keywords: Palladium(II) cyclometallated complexes; Crystal and molecular structures; Ammonium hexafluorophosphate; Chelating; Phosphines

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1. Introduction

Cyclometallated compounds [1–5] are formed when an organic ligand links to a metal center through a σM–C bond and additional bonding of the metal via an appropriate donor atom completes the stable, more often than not five-membered, metallated ring. Their applications are widespread throughout the chemical family, ranging from organic and organometallic chemistry [6–9], to bioactive species [10] and catalytic processes [11].

Although bidentate nitrogen-donor ligands may undergo double metallation to give compounds with two σM–C bonds and with coordination of each nitrogen atom to different metal centers [12–16], the reaction conditions may influence the metallation process, thus altering the number of M–N, as well as M–C, bonds in the final compound. We have reported that bidentate Schiff bases derived from dialdehydes, such as 1,4-$(CyN{=}CH)_2C_6H_4$ and 1,3-$(CyN{=}CH)_2C_6H_4$, react with palladium(II) acetate in glacial acetic acid to give only monocyclometallated complexes after cleavage of one C=N double bond [17,18] and we have also been interested in the study of the reactivity of these complexes towards nucleophiles such as tertiary mono- and diphosphines [19]. In either case, the parent chloro-bridged dinuclear compound, such as **2**, undergoes scission of the Pd_2Cl_2 unit to render mononuclear

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species. In the former case, compounds with terminal Pd–Cl bonds and with the palladium atom bonded to four different atoms are produced, whereas in the latter, the chlorine ligands are lost completely and 1:1 electrolyte species are formed with the diphosphine acting as a chelating ligand. In spite that functionalized palladium(II) compounds, i.e. those bearing a non-coordinated formyl unit, researched by us have been fully characterized [18], X-ray crystal diffraction data have been somewhat limited and in the present paper we report the crystal and molecular structures of three functionalized palladium(II) cyclometallated complexes.

2. Experimental

2.1. General procedures

The synthesis of complexes **1**–**4** has been reported previously [18,19]. Solvents were purified by standard methods [20]. Chemicals were reagent grade. The phosphines $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2P(CH_2)_2PPh_2$ (dppe) 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 $SiMe_4$ (^1H, $^{13}C-\{^1H\}$) or 85% H_3PO_4 ($^{31}P-\{^1H\}$) and were recorded on Bruker WM-250, AMX-300 and AMX-500 spectrometers. All chemical shifts were reported downfield from standards.

2.1.1. *[Pd{3-(CHO)C$_6$H$_3$C(H)=NCy}{Ph$_2$PCH$_2$PPh$_2$-P,P}][PF$_6$]* **5**

To a suspension of **2** (50 mg, 0.070 mmol) in acetone (ca. 15 cm^3), $Ph_2PCH_2PPh_2$ (54 mg, 0.140 mmol) was added and the resulting solution stirred for 2 h, after which ammonium hexafluorophosphate was added and the resulting suspension stirred for another 2 h; water (ca. 15 cm^3) was then added and the resulting mixture stirred for a further 2 h, the orange precipitate formed was filtered off, dried in vacuo and recrystallized from dichloromethane–hexane. Yield 58%. *Anal*. Found: C, 55.6; H, 5.0; N, 1.6. Calc. for $C_{39}H_{38}F_6NOP_3Pd$: C, 55.1; H, 4.5; N, 1.6%. IR: ν(C=O) 1693m, ν(C=N) 1617w cm^{-1}. ^1H NMR ($CDCl_3$, δ ppm, J Hz): 9.85 [s, 1H, HC=O], 8.35 [d, 1H, HC=N, J(PHi) = 8.4], 7.90[d, 1H, H^2, $J(H^2H^4) = 1.8$], 6.89 [m, 1H, H^5, $J(H^4H^5) = 8.3$, $J(PH^5 = 5.4]$, 4.32 [dd, 2H, PCH_2P, J(PH) = 10.7, 11.2]. $^{31}P-\{^1H\}$ NMR ($CDCl_3$, δ ppm) −6.0 [d, J(PP) = 66.5], −29.4d, −145.9 [h, PF_6^-].

Complex **6** was prepared similarly as a white solid.

2.1.2. *[Pd{3-(CHO)C$_6$H$_3$C(H)=NCy}{Ph$_2$P(CH$_2$)$_2$PPh$_2$-P,P}][PF$_6$]* **6**

Yield 77%. *Anal*. Found: C, 54.9; H, 4.5; N, 1.4. Calc. for $C_{40}H_{40}F_6NOP_3Pd$: C, 55.1; H, 4.7, N, 1.6%. IR: ν(C=O) 1694m, ν(C=N) 1618w cm^{-1}. ^1H NMR ($CDCl_3$, δ ppm, J Hz): 9.83 [s, 1H, HC=O], 8.46 [d, 1H, HC=N, J(PHi) = 8.6], 7.92[d, 1H, H^2, $J(H^2H^4) = 1.8$], 6.85 [m, 1H, H^5, $J(H^4H^5) = 8.0$]. $^{31}P-\{^1H\}$ NMR ($CDCl_3$, δ ppm) 61.8 [d, J(PP) = 26.3], 45.9d, −146.1 [m, PF_6^-].

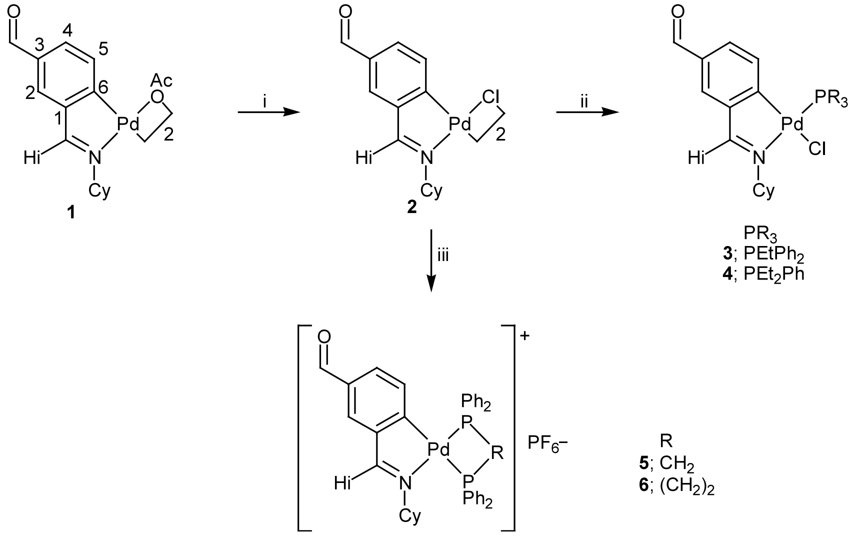
2.1.3. X-ray crystallographic study

For compound **1** three dimensional, room temperature (r.t.) X-ray data were collected on a Siemens P4 diffractometer in the range $3.6° < \theta < 45°$ by the ω scan method. The 9528 reflections measured were corrected for Lorentz and polarization effects (but not for absorption). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with allowance for thermal anisotropy of all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0961$ (observed data, F) and $wR_2 = 0.3244$ (F^2, 8286 unique data, 757 parameters). The structure solution and refinement were carried out using the program package SHELX-97 [21].

Crystals of complexes **3** and **4** were mounted on a glass fiber and transferred to a Bruker SMART CCD single-crystal X-ray dffractometer. Three-dimensional, r.t. X-ray data were collected by the ω scan method using graphite-monochromated Mo Kα radiation. All the 14 146 (**3**) and 12 553 (**4**) measured reflections were corrected for Lorentz and polarization effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections (transmissions max./min. 0.947/0.757 and 0.963/0.638 for complexes **3** and **4**, respectively). 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 $R = 0.0313$ and 0.0419 (for complexes **3** and **4**, respectively, observed data, F) and $wR_2 = 0.0808$ and 0.928 (for complexes **3** and **4**, respectively; F^2, 6417 and 4995 unique data, 298 and 264 parameters), with allowance for thermal anisotropy of all non-hydrogen atoms. The structure solution and refinement were carried out using the program package SHELX-97 [21].

3. Results and discussion

In previous papers we described the preparation of complexes **1**–**4** [18,19], however, these have been included to complete the reaction sequence which is shown in Scheme 1. Compounds **5** and **6** were characterized by elemental analysis (C, H, N) and by IR, ^1H



Scheme 1. (i) NaCl (acetone–water); (ii) PR$_3$ (acetone 1:2 molar ratio; (iii) dppm or dppe (acetone 1:2 molar ratio).

and ^{31}P–{^{1}H} NMR spectroscopy (data in the Section 2).

3.1. Crystal structure of [Pd{3-(CHO)C$_6$H$_3$C(H)=NCy}(μ-O$_2$CMe)]$_2$, 1

Crystals were grown by slowly evaporating a dichloromethane–*n*-hexane solution of the complex. The molecular structure is illustrated in Fig. 1. Crystal data are given in Table 1 and selected bond distances and angles with e.s.d. are shown in Table 2.

The crystal of complex **1** consists of discrete molecules separated by van der Waals distances. The asymmetric unit contains two molecules of **1** having similar structures, of which only one will be discussed here.

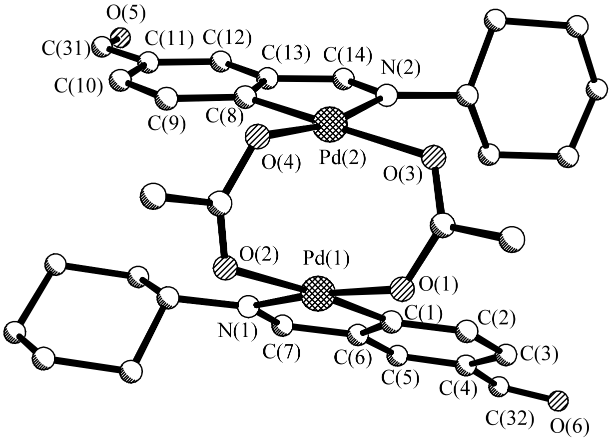


Fig. 1. Molecular structure of [Pd{3-(CHO)C$_6$H$_3$C(H)=NCy}(μ-O$_2$CMe)]$_2$, **1**, with labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 1
Crystallographic data for complexes **1**, **3** and **4**

	1	**3**	**4**
Chemical formula	$C_{32}H_{38}N_2O_6Pd_2$	$C_{28}H_{31}ClNOPPd$	$C_{24}H_{31}ClNOPPd$
Formula weight	759.45	570.36	522.32
T (°C)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a (Å)	13.410(5)	8.599(17)	11.692(3)
b (Å)	15.901(6)	12.200(3)	13.876(4)
c (Å)	16.242(8)	24.810(3)	15.096(4)
α (°)	93.61(4)		
β (°)	90.67(3)	94.89(2)	93.111(5)
γ (°)	109.71(2)		
V (Å^3)	3252(3)	2593.4(9)	2445(11)
Z	4	4	4
μ (mm^{-1})	1.150	0.901	0.948
Reflections collected	9528	14 146	12 553
Unique reflections	8291 ($R_{int} = 0.114$)	6417 ($R_{int} = 0.023$)	4995 ($R_{int} = 0.045$)
R_1 [a]	0.0961	0.0313	0.0419
wR_2 [b]	0.3244	0.0808	0.0928

[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.

Each molecule may be described as a dimer with the *anti* conformation and the cyclometallated fragments in the characteristic open-book disposition, linked by two acetate-bridging ligands. The palladium atoms are bonded to the Schiff base ligand through a phenyl carbon atom and the imine nitrogen atom and to two oxygen atoms from the acetate-bridging ligands, in a slightly distorted square-planar disposition.

The angles in the coordination sphere of palladium are close to the expected value of 90°, with the most noticeable distortions corresponding to the C(1)–Pd(1)–

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**

Bond lengths			
Pd(1)–C(1)	1.94(2)	Pd(1)–N(1)	2.020(12)
Pd(1)–O(1)	2.041(11)	Pd(1)–O(2)	2.147(12)
Pd(1)–Pd(2)	2.929(2)	Pd(2)–C(8)	1.95(2)
Pd(2)–N(2)	2.029(12)	Pd(2)–O(4)	2.061(11)
Pd(2)–O(3)	2.175(11)	Pd(1A)–C(1A)	1.95(2)
C(1)–C(6)	1.44(2)	C(8)–C(13)	1.41(2)
C(6)–C(7)	1.43(2)	C(13)–C(14)	1.44(2)
C(7)–N(1)	1.31(2)	C(14)–N(2)	1.30(2)
Pd(1A)–N(1A)	2.015(13)	Pd(1A)–O(1A)	2.034(11)
Pd(1A)–O(2A)	2.168(12)	Pd(1A)–Pd(2A)	2.894(2)
Pd(2A)–C(8A)	1.96(2)	Pd(2A)–N(2A)	2.025(13)
Pd(2A)–O(4A)	2.051(12)	Pd(2A)–O(3A)	2.174(12)
C(1A)–C(6A)	1.39(2)	C(8A)–C(13A)	1.43(2)
C(6A)–C(7A)	1.46(2)	C(13A)–C(14A)	1.45(2)
C(7A)–N(1A)	1.24(2)	C(14A)–N(2A)	1.27(2)
Bond angles			
C(1)–Pd(1)–N(1)	82.8(6)	C(1)–Pd(1)–O(1)	92.6(6)
N(1)–Pd(1)–O(1)	174.2(5)	C(1)–Pd(1)–O(2)	176.0(6)
N(1)–Pd(1)–O(2)	95.5(5)	O(1)–Pd(1)–O(2)	88.9(5)
C(8)–Pd(2)–N(2)	81.7(6)	C(8)–Pd(2)–O(4)	93.1(6)
N(2)–Pd(2)–O(4)	169.9(5)	C(8)–Pd(2)–O(3)	178.7(5)
N(2)–Pd(2)–O(3)	97.0(5)	O(4)–Pd(2)–O(3)	88.3(5)
C(6)–C(1)–Pd(1)	112.6(11)	C(13)–C(8)–Pd(2)	114.4(12)
C(7)–C(6)–C(1)	114.1(14)	C(8)–C(13)–C(14)	113.0(2)
N(1)–C(7)–C(6)	117.0(2)	N(2)–C(14)–C(13)	119.0(2)
C(7)–N(1)–Pd(1)	113.3(11)	C(14)–N(2)–Pd(2)	112.6(10)
C(1A)–Pd(1A)–N(1A)	81.0(6)	C(1A)–Pd(1A)–O(1A)	94.8(6)
N(1A)–Pd(1A)–O(1A)	173.9(5)	C(1A)–Pd(1A)–O(2A)	175.2(6)
N(1A)–Pd(1A)–O(2A)	97.1(5)	O(1A)–Pd(1A)–O(2A)	86.8(5)
C(8A)–Pd(2A)–N(2A)	81.6(6)	C(8A)–Pd(2A)–O(4A)	92.6(6)
N(2A)–Pd(2A)–O(4A)	173.8(5)	C(8A)–Pd(2A)–O(3A)	178.2(6)
N(2A)–Pd(2A)–O(3A)	98.6(5)	O(4A)–Pd(2A)–O(3A)	87.1(5)
C(6A)–C(1A)–Pd(1A)	112.9(12)	C(13A)–C(8A)–Pd(2A)	112.5(11)
C(7A)–C(6A)–C(1A)	114.3(14)	C(8A)–C(13A)–C(14A)	113.7(14)
N(1A)–C(7A)–C(6A)	115.8(14)	N(2A)–C(14A)–C(13A)	117.0(14)
C(7A)–N(1A)–Pd(1A)	115.9(11)	C(14A)–N(2A)–Pd(2A)	114.8(11)

N(1) and C(8)–Pd(2)–N(2) angles of 82.8(6)° and 81.7(6)°, respectively, consequent upon chelation. This is also shown by the value of the C(2)–C(1)–Pd(1) and C(9)–C(8)–Pd(2) bond angles of 130.7(14)° and 128.5(12)°, respectively, considerably larger than the theoretical 120°. The Pd(1)–Pd(2) bond length of is noticeably larger than the sum of the covalent radii for two square-planar palladium(II) atoms [22], thus precluding any Pd···Pd interaction.

The Pd(1)–C(1) and Pd(2)–C(8) bond distances are somewhat shorter than the values predicted from their covalent radii [22], but similar to values found earlier [23,24]. However, the Pd(1)–N(1) and Pd(2)–N(2) bond lengths are in agreement with the value based on the sum of covalent radii for nitrogen and palladium [22] and similar to values reported previously [23,24]. The differing Pd(1)–O(1) and Pd(1)–O(2), and Pd(2)–O(4) and Pd(2)–O(3) bond distances reflect the higher *trans* influence of the aryl carbon as compared with the imine nitrogen atom. The remaining bond distances and bond angles of the metallacycle are in accordance with reported values [23,24]. The proximity of the Schiff bases due to the dimeric nature of the complex leads to inter-ligand repulsions on the open side of the molecule, which results in the coordination planes of the palladium atoms being tilted at an angle of 33.7°.

In spite of these repulsions, the cyclometallated rings (plane 1) are planar and almost coplanar with the palladium coordination plane (plane 2) and with the metallated phenyl rings (plane 3) [angles between planes are as follow: plane 1/2, 2.7°; plane 1/3, 2.2°; plane 2/3, 4.4°; planes to Pd(1)]. The high *R* values are probably due to the quality of the crystal; we were unable to grow a better specimen.

3.2. *Crystal structures of [Pd{3-(CHO)C_6H_3C(H)=NCy}(Cl)(PEtPh_2)],* **3** *and [Pd{3-(CHO)C_6H_3C(H)=NCy}(Cl)(PEt_2Ph)],* **4**

Suitable crystals were grown by slowly evaporating chloroform solutions of the complexes. The molecular structures are illustrated in Figs. 2 and 3. Crystal data are given in Table 1 and selected bond distances and angles with e.s.d. are shown in Table 3.

The crystals of complexes **3** and **4** consist of discrete molecules separated by van der Waals distances. The geometry around the palladium atom may be regarded as slightly distorted square-planar, with the Pd(II) bonded to the C(1) carbon and the N(1) nitrogen atoms of the Schiff base ligand, to the Cl(1) chlorine and to the P(1) phosphorus atom of the tertiary monophosphine

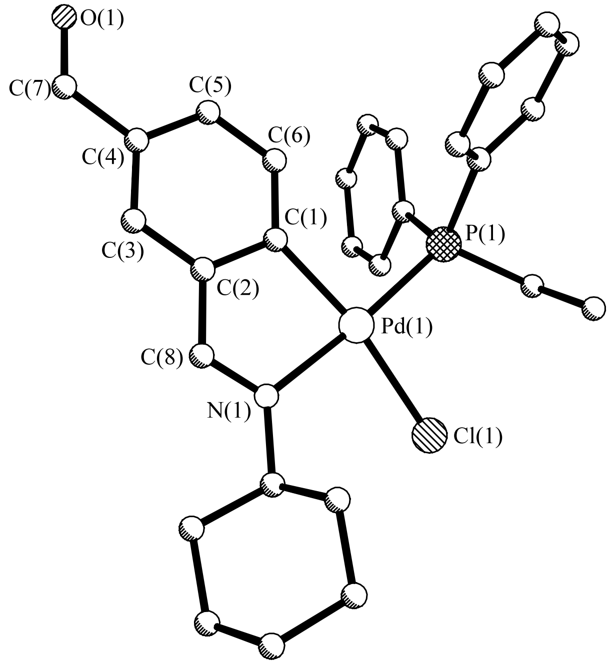


Fig. 2. Molecular structure of [Pd{3-(CHO)C_6H_3C(H)=NCy}(Cl)(PEtPh_2)], **3**, with labeling scheme. Hydrogen atoms have been omitted for clarity.

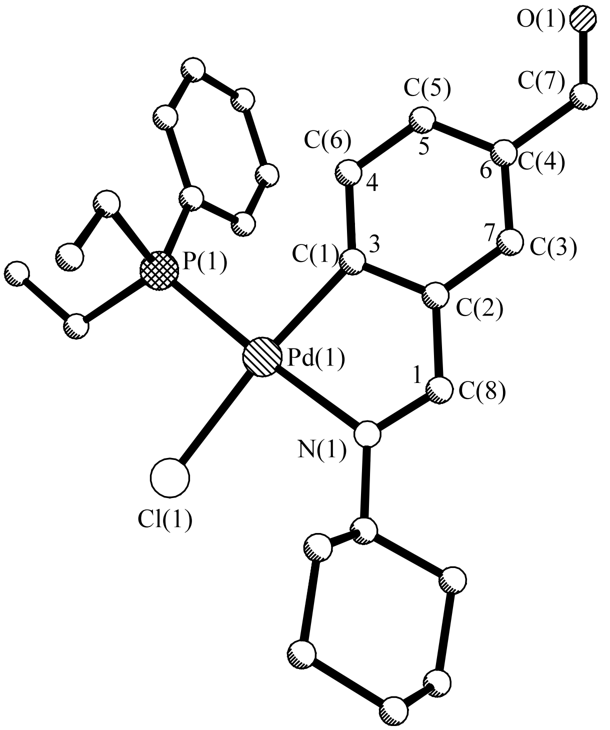


Fig. 3. Molecular structure of $[Pd\{3\text{-}(CHO)C_6H_3C(H)=NCy\}(Cl)(PEt_2Ph)]$, **4**, with labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) for complexes **3** and **4**

	3	4
Bond lengths		
Pd(1)–C(1)	2.010(2)	2.019(4)
Pd(1)–N(1)	2.117(2)	2.115(3)
Pd(1)–Pd(1)	2.2668(7)	2.258(1)
Pd(2)–Cl(2)	2.3698(7)	2.359(1)
C(1)–C(2)	1.410(3)	1.408(6)
C(2)–C(8)	1.456(3)	1.457(6)
N(1)–C(8)	1.273(3)	1.267(5)
Bond angles		
C(1)–Pd(1)–N(1)	81.15(8)	81.3(2)
C(1)–Pd(1)–P(1)	94.37(7)	95.2(1)
N(1)–Pd(1)–P(1)	175.05(5)	176.1(1)
C(1)–Pd(1)–Cl(1)	168.61(7)	174.1(1)
N(1)–Pd(1)–Cl(1)	92.95(6)	93.0(1)
P(1)–Pd(1)–Cl(1)	91.82(3)	90.54(5)
C(2)–C(1)–Pd(1)	111.61(61)	110.9(3)
C(1)–C(2)–C(8)	116.5(2)	116.9(4)
C(8)–N(1)–Pd(1)	112.58(16)	112.3(3)
N(1)–C(8)–C(2)	118.0(2)	118.2(4)

ligand. The sum of the angles about the palladium atoms is approximately 360° as expected for a square-planar geometry. The donor atoms of the chelating Schiff base, occupying mutually *cis* positions force a bite angle of 81.15(8)° and 81.3(2)° for complexes **3** and **4**, respectively, somewhat smaller than the expected 90°.

The Pd(1)–C(1) bond lengths are shorter than the expected value of 2.081 Å based on the sum of the covalent radii for carbon and palladium [22], but similar to other values reported [19,25,26]. However, the Pd(1)–N(1) bond distances are considerably longer than the expected value of 2.01 Å [22]. These values show the high *trans* influence of the phosphine ligand [cf. with the Pd–N bond length values in compound **1**]. The Pd(1)–P(1) bond distances are within the expected values [19,26]. The Pd(1)–Cl(1) distances are somewhat longer than the expected values based on the sum of the covalent radii [22], due to the *trans* influence of the C(1) phenyl carbon atom. The C=N distances are consistent with those found earlier in other cyclometallated complexes [15].

The geometry around the palladium atom is planar [Pd(1), C(1), N(1), P(1), Cl(1), plane 1; mean deviation from the plane: 0.096 (**3**), 0.024 Å (**4**)] and almost coplanar with the cyclometallated [Pd(1), C(1), C(2), C(8), N1(1), plane 2; mean deviation from the plane: 0.018 (**3**), 0.036 Å (**4**)] and phenyl [C(1)–C(6), plane 3; mean deviation from the plane: 0.038 (**3**), 0.011 Å (**4**)] rings [angles between planes; plane 1/2: 7.0° (**3**), 3.3° (**4**); plane 1/3: 9.8° (**3**), 6.2° (**4**); plane 2/3: 2.9° (**3**), 4.7° (**4**)].

3.3. Cyclometallated complexes with diphosphine ligands

Reaction of the chloro-bridged complex **2** with the tertiary diphosphines $PPh_2CH_2PPh_2$ (dppm) and $PPh_2(CH_2)_2PPh_2$ (dppe) in a 1:2 molar ratio, and ammonium hexafluorophosphate, yielded the mononuclear cyclometallated complexes $[Pd\{3\text{-}(CHO)C_6H_3C(H)=NCy\}\{Ph_2PCH_2PPh_2\text{-}P,P\}][PF_6]$, **5** and $[Pd\{3\text{-}(CHO)C_6H_3C(H)=NCy\}\{Ph_2P(CH_2)_2PPh_2\text{-}P,P\}][PF_6]$, **6**, which were fully characterized (see Section 2). The IR spectra of the complexes showed the band assigned to the free formyl group at approximately 1693 cm^{-1} and the band corresponding to the $\nu(C=N)$ stretch at approximately 1618 cm^{-1}, the latter shifted toward lower wavenumbers, as compared with the non-coordinated ligand, due to Pd–N coordination [27,28]. The IR spectra also showed the absence of the $\nu(Pd–Cl)$ bands. In the ^1H NMR spectra the HC=N resonance signal showed coupling to only one of the phosphorus nuclei [J(PH) ca. 8.5 Hz], presumably that *trans* to it. The ^1H NMR spectra also showed the singlet resonance corresponding to the HC=O proton approximately δ9.83. The $^{31}P\text{–}\{^1H\}$ spectra showed two doublets [$J(PP) = 66.5$ and 26.3 Hz for complexes **5** and **6**, respectively] for the two inequivalent phosphorus nuclei. The assignment of the doublets was made in accordance with the assumption that a ligand of greater *trans* influence shifts the resonance of the phosphorus atoms *trans* to it to lower frequency [29].

4. Supplementary data

Full details of data collection and structure refinement have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 184330 (**1**), 184331 (**3**) and 184332 (**4**). 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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