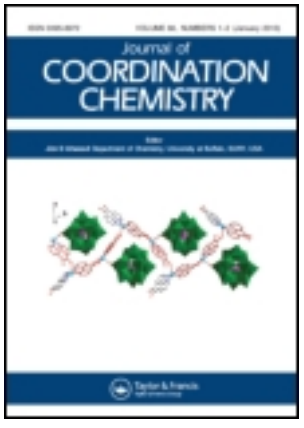


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis and characterization of cyclometallated palladium(II) complexes with 2-(diphenylphosphino)benzaldehyde

Gregorio Sánchez [a], Joaquín García [a], Malva Liu [b], Luis García [c], José Pérez [c], Eduardo Pérez [c] & José L. Serrano [c]

[a] Departamento de Química Inorgánica, Universidad de Murcia, Murcia, Spain

[b] Departamento de Termodinámica, Universidad de Valencia, Burjassot (Valencia), Spain

[c] Departamento de Ingeniería Minera, Geológica y Cartográfica. Área de Química Inorgánica, Campus Mare Nostrum, Universidad Politécnica de Cartagena, Cartagena, Spain

Accepted author version posted online: 20 Jun 2013.Published online: 24 Jul 2013.

To cite this article: Gregorio Sánchez, Joaquín García, Malva Liu, Luis García, José Pérez, Eduardo Pérez & José L. Serrano (2013) Synthesis and characterization of cyclometallated palladium(II) complexes with 2-(diphenylphosphino)benzaldehyde, Journal of Coordination Chemistry, 66:16, 2919-2929, DOI: 10.1080/00958972.2013.817572

To link to this article: http://dx.doi.org/10.1080/00958972.2013.817572

Journal of Coordination Chemistry, 2013
Vol. 66, No. 16, 2919–2929, http://dx.doi.org/10.1080/00958972.2013.817572

Synthesis and characterization of cyclometallated palladium (II) complexes with 2-(diphenylphosphino)benzaldehyde

GREGORIO SÁNCHEZ†, JOAQUÍN GARCÍA†, MALVA LIU‡, LUIS GARCÍA§, JOSÉ PÉREZ§, EDUARDO PÉREZ§ and JOSÉ L. SERRANO*§

†Departamento de Química Inorgánica, Universidad de Murcia, Murcia, Spain
‡Departamento de Termodinámica, Universidad de Valencia, Burjassot (Valencia), Spain
§Departamento de Ingeniería Minera, Geológica y Cartográfica. Área de Química Inorgánica, Campus Mare Nostrum, Universidad Politécnica de Cartagena, Cartagena, Spain

(*Received 13 February 2013; in final form 15 May 2013*)

New palladium(II) complexes containing 2-(diphenylphosphino)benzaldehyde **a** ($Ph_2P(o\text{-}C_6H_4CHO)$, displaying different coordination modes, have been synthesized in moderate to good yields (62–91%). The cyclometallated palladium(II) complexes $[Pd(C\hat{}N)(Ph_2\mathbf{P}(o\text{-}C_6H_4CHO)(Cl)]$ (**1–4**) in which **a** is P-monodentate have been prepared by reacting it with selected cyclometallated precursors containing bridging chlorides $[Pd(C\hat{}N)(\mu\text{-}Cl)]_2$ [C^N=2-phenylpyridine (Phpy), 7,8-benzoquinoline (Bzq), azobenzene (Phazo), and 2-phenyloxazoline (Phox), respectively]. A rigid P,O-chelating behavior of **a**, confirmed by the crystal structure determination of $[Pd(Phox)(Ph_2\mathbf{P}(o\text{-}C_6H_4CH\mathbf{O})][CF_3SO_3]$ (**8**), is observed in complexes (**5–8**) obtained by adding $AgCF_3SO_3$ in 2: 1 ratio to $[Pd(C\hat{}N)(\mu\text{-}Cl)]_2$ precursors. NMR spectroscopy helped identify the proposed coordination modes, with noticeable shifts of resonances upon chelation: upfield in the case of ^{31}P and CHO in ^{1}H, downfield for the C=O signal in ^{13}C NMR. All the new complexes have been characterized by partial elemental analyses and spectroscopic methods (IR, fast atom bombardment, ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR).

Keywords: Cyclometallated palladium(II) complexes; 2-(Diphenylphosphino)benzaldehyde; Hemilabile properties; Crystal structure

1. Introduction

Ligands that contain dissimilar chemical functions [1–5], such as soft phosphine and hard N or O donors, have attracted considerable interest mainly due to their versatile coordination behavior [6–9] and potential hemilability [3–5, 10]. Interesting applications of these properties have been the "weak-link approach" [11] or the use of some ligands and complexes in chemical sensing [12] and catalytic processes [13] in which the hard donor dissociates readily from soft metal centres, generating a vacant site on the metal ion for substrate binding. Both ligand design and studies about the conditions in which the different bonding patterns may take place, like the one we present here, are of considerable

*Corresponding author. Email: jose.serrano@upct.es

importance to understand and make use of the properties exhibited by ligands and complexes.

N^P-ligands are the most abundant type of hybrid ligands [13]. Among them, iminophosphine ligands prepared by condensation of 2-(diphenylphosphino)benzaldehyde with primary amines (*o*-$Ph_2PC_6H_4CH$=N-R) and its complexes have found interesting applications [14] since first reported in the early nineties [15]. We have described the syntheses of some organometallic derivatives containing iminophosphine ligands, either with an ortho-metallated palladium(II) backbone [16], pentafluorophenyl derivatives of Ni(II) and Pd(II) [17] or just coordination compounds bearing N^P-/NPO-ligands [18]. It is surprising that the chemistry of the unit employed to prepare such variety of ligands with interesting properties, 2-(diphenylphosphino)benzaldehyde, has not been explored, given that it is capable of behaving as potential P-donor or P^O-chelate [19]. In fact, only a few articles have described to date its chemistry coordinating palladium [20] and just four crystal structures have been reported, as found in CSD version 5.33 (November 2011 updates Feb–May–Aug 2012; Refcodes: QARPOP, YIKTOC, UZEBIL, and UZEBEH).

As mentioned above in general for hemilabile ligands, studies about the conditions in which 2-(diphenylphosphino)benzaldehyde can act as P-monodentated or P^O-chelate are of interest and have been directly related with applications in catalysis of, for example, its Pd [20a] and Ru [21] complexes.

We present here the synthesis and characterization of new 2-(diphenylphosphino) benzaldehyde derivatives of palladium(II) in which this ligand adopts different coordination modes depending on the reaction conditions with classical orthometallated halide-bridged dimers.

2. Experimental

2.1. *Material and measurements*

C, H, and N analyses were carried out with a Carlo Erba instrument. IR spectra were recorded on a PerkinElmer spectrophotometer 16F PC FT-IR using Nujol mulls between polyethylene sheets. NMR data (^1H, ^{13}C, ^{31}P, ^{19}F) were recorded on Bruker Avance 200 or 300 spectrometers. Mass spectrometric analyses were performed on a Fisons VG Autospec double-focusing spectrometer, operated in negative mode. Ions were produced by fast atom bombardment (FAB) with a beam of 25-KeV Cs atoms. The mass spectrometer was operated with an accelerating voltage of 8 kV and a resolution of at least 1000.

The cyclometallated precursors $[Pd(C^N)(\mu\text{-}Cl)]_2$ [C^N=2-phenylpyridine (Phpy), 7,8-benzoquinoline (Bzq), azobenzene (Phazo), and 2-phenyloxazoline (Phox)] were prepared as described [22]. Commercially available chemicals were purchased from Aldrich Chemical Co., and used without purification; all solvents were dried by standard methods before use.

2.2. *X-ray crystallography*

Crystals suitable for diffraction were prepared by slow diffusion of hexane into CH_2Cl_2 solutions. Crystallographic data are summarized in table 1. For **8,** data collection was performed at 293 K on a Nonius Kappa-CCD single-crystal diffractometer. Crystal-detector distance was fixed at 35 mm, and a total of 122 images were collected using the oscillation method, with scan angle per frame, 2° oscillation and 20 s exposure time per image. Data

Table 1. Crystallographic data for **8**.

Complex	**8** (deposit CCDC 924213)
Formula	$C_{29}H_{23}F_3NO_5PPdS$
Formula weight	691.91
Crystal system	Monoclinic
Space group	*P21/c*
Unit cell dimensions (Å, °)	
a	8.9780(2)
b	21.6710(6)
c	14.8610(5)
α	90
β	107.6800(10)
γ	90
Volume (Å^3), *z*	2754.82(13), 4
Calculated density (g cm^{-3})	1.668
μ (mm^{-1})	0.869
R_{int}	0.0580
R_1 ($I > 2\sigma(I)$)	0.1353
ωR_2 (all data)	0.1426
Goodness-of-fit on F^2	0.997

collection strategy was calculated with the program collect [23]. Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack [24].

The structure was solved by direct methods [25] and refined by full-matrix least-squares using anisotropic thermal parameters for non-H atoms [25] (table 1). Hydrogens were introduced in calculated positions and refined during the last stages of the refinement. CCDC reference number 924213 contains the Supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

2.3. *Synthesis*

*Complexes [Pd(C^N)(Ph$_2$**P**(o-C$_6$H$_4$CHO)(Cl)] [C^N=2-phenylpyridine (Phpy) **1**, 7,8-benzoquinoline (Bzq) **2**, azobenzene (Phazo) **3**, and 2-phenyloxazoline (Phox) **4**]*

The new complexes were obtained by treating [Pd(C^N)(μ-Cl)]$_2$ with 2-(diphenylphosphino)benzaldehyde in molar ratio 1 : 2 using CH_2Cl_2 as solvent and according to the following general method. To a dichloromethane suspension (10 mL) of the corresponding precursor [Pd(C^N)(μ-Cl)]$_2$ (100 mg; 0.168, 0.156, 0.155; and 0.174 mM, respectively) was added the stoichiometric amount of solid 2-(diphenylphosphino)benzaldehyde. The resulting solution was stirred for 60 min, filtered through a short celite column and then concentrated to half volume under reduced pressure. Addition of ether caused precipitation of the new complexes, which were filtered off, air-dried, and recrystallized from dichloromethane-hexane.

[Pd(Phpy)(Ph$_2$**P**(*o*-C$_6$H$_4$CHO)(Cl)] (**1**) (yield: 179 mg; 91%). Anal. Calcd for $C_{30}H_{23}ClNOPPd$ (%): C, 61.4; H, 3.9; N, 2.4. Found: C, 61.2; H, 4.1; N, 2.7. IR Nujol mull (ν_{max}, cm^{-1}: 1698(s), 1682(s), 1602(s), 1580(s). ^{1}H NMR (200 MHz; $CDCl_3$) δ_H: 10.51 (1H, d, CHO, J = 2.6 Hz); 9.61 (1H, m, arom); 7.91 (6H, m, arom); 7.76 (1H, d, arom, J = 7.6 Hz); 7.46–7.34 (9H, m, arom); 7.23 (1H, m, arom); 6.99 (2H, m, arom); 6.56 (2H, m, arom). ^{13}C NMR (50.3 MHz; $CDCl_3$) δ_C: 189.7 (d, CHO, J_{PC} = 36.6 Hz); 164.7 (d, Phpy, J_{PC} = 12.0 Hz); 154.3 (s, O^P ligand); 150.7 (s, Phpy); 147.4 (s, Phpy); 139.2–118.3 (C_6H_5, C_6H_4). ^{31}P NMR (121.49 MHz; $CDCl_3$) δ_P: 38.3 (s). FAB-MS (positive mode) *m/z*: 550 (M^+–Cl).

[Pd(Bzq)(Ph$_2$**P**(*o*-C$_6$H$_4$CHO)(Cl)] (**2**) (yield: 118 mg; 62%). Anal. Calcd for $C_{32}H_{23}ClNOPPd$ (%): C, 63.0; H, 3.8; N, 2.3. Found: C, 63.3; H, 4.1; N, 2.6. IR Nujol

mull (ν_{max}, cm^{-1}: 1698(s), 1694(s), 1568(s). ^1H NMR (300 MHz; $CDCl_3$) δ_H: 10.47 (1H, d, CHO, $J = 1.4$ Hz); 9.75 (1H, m, arom); 8.25 (1H, dd, $J_{HH} = 5.4$; $J_{Hp} = 0.6$ Hz); 7.97 (5H, m, arom); 7.65 (1H, d, $J_{HH} = 5.2$ Hz); 7.45–7.04 (11H, m, arom); 6.90 (1H, dd, $J_{HH} = 8.1$; $J_{Hp} = 7.0$ Hz); 6.86 (1H, m, arom); 6.72 (1H, m, arom). ^{13}C NMR (75.47 MHz; $CDCl_3$) δ_C: 189.5 (d, CHO, $J_{PC} = 36.3$ Hz); 154.4 (d, Bzq, $J_{PC} = 12.0$ Hz); 152.7 (s, O^P ligand); 149.8 (s, Bzq); 142.8 (s, Bzq); 137.9–121.5 (C_6H_5, C_6H_4). ^{31}P NMR (121.49 MHz; $CDCl_3$) δ_P: 39.4 (s). FAB-MS (positive mode) *m/z*: 574 (M^+–Cl).

[Pd(Phazo)(Ph_2**P**(*o*-C_6H_4CHO)(Cl)] (**3**) (yield: 150 mg; 79%). Anal. Calcd for $C_{31}H_{24}ClN_2OPPd$ (%): C, 60.7; H, 3.9; N, 4.6. Found: C, 60.4; H, 4.0; N, 4.9 IR Nujol mull (ν_{max}, cm^{-1}: 1701(s), 1680(s), 1575(s). ^1H NMR (300 MHz; $CDCl_3$) δ_H: 10.15 (1H, d, CHO, $J = 1.8$ Hz); 7.95 (1H, d, $J = 7.2$ Hz) 7.85 (7H, m, arom); 7.54–7.21 (11H, m, arom); 7.06 (1H, m, arom); 6.94 (1H, dd, $J_{HH} = 7.8$; $J_{Hp} = 7.0$ Hz); 6.64 (1H, m, arom); 6.53 (1H, m, arom). ^{13}C NMR (75.47 MHz; $CDCl_3$) δ_C: 190.2 (d, CHO, $J_{PC} = 24.4$ Hz); 165.5 (s, Phazo); 156.7 (s, O^P ligand); 151.8 (d, Phazo, $J_{PC} = 18.6$ Hz); 137.5–124.2 (C_6H_5, C_6H_4). ^{31}P NMR (121.49 MHz; $CDCl_3$) δ_P: 40.4 (s). FAB-MS (positive mode) *m/z*: 577 (M^+–Cl).

[Pd(Phox)(Ph_2**P**(*o*-C_6H_4CHO)(Cl)] (**4**) (yield: 129 mg; 64%). Anal. Calcd for $C_{28}H_{23}ClNO_2PPd$ (%): C, 58.1; H, 4.0; N, 2.4. Found: C, 58.4; H, 4.3; N, 2.5. IR Nujol mull (ν_{max}, cm^{-1}: 1698(s), 1682(s), 1580(s). ^1H NMR (200 MHz; $CDCl_3$) δ_H: 10.65 (1H, d, CHO, $J = 1.2$ Hz); 8.76 (1H, m, arom); 7.85 (4H, m, arom); 7.58 (1H, m, arom); 7.45–7.30 (8H, m, arom); 7.22 (1H, m, arom); 6.85 (1H, m, arom); 6.58 (1H, m, arom); 6.40 (1H, m, arom); 4.73 (2H, t, -CH_2–, $J = 9.6$ Hz); 4.19 (2H, t, –CH_2–, $J = 9.6$ Hz). ^{13}C NMR (50.3 MHz; $CDCl_3$) δ_C: 191.2 (d, CHO, $J_{PC} = 25.0$ Hz); 177.6 (s, Phox); 153.0 (s, O^P ligand); 151.0 (s, Phox); 138.0–124.1 (C_6H_5, C_6H_4); 70.8 (s, Phox); 51.9 (s, Phox). ^{31}P NMR (121.49 MHz; $CDCl_3$) δ_P: 38.4 (s). FAB-MS (positive mode) *m/z*: 542 (M^+–Cl).

*Complexes [Pd(C^N)(Ph_2**P**(*o*-C_6H_4CH**O**)] [CF_3SO_3] [C^N= 2-phenylpyridine (Phpy)* ***5****, 7,8-benzoquinoline (Bzq)* ***6****, azobenzene (Phazo)* ***7****, and 2-phenyloxazoline (Phox)* ***8****]*

The complexes were obtained by treating [Pd(C^N)(μ-Cl)]$_2$ with 2-(diphenylphosphino) benzaldehyde in molar ratio 1 : 2 using CH_2Cl_2 as solvent and according to the following general method. To a CH_2Cl_2 suspension (10 mL) of the precursor [Pd(C^N)(μ-Cl)]$_2$ (100 mg; 0.168; 0.156; 0.155; and 0.174 mM, respectively) was added the stoichiometric amount of solid 2-diphenylphosphino)benzaldehyde and Ag(CF_3SO_3). After stirring under reflux for 30 min, the solution was filtered through celite to remove AgCl and then concentrated under reduced pressure to half volume. Addition of diethyl ether caused precipitation of the new complexes, which were filtered off, air-dried, and recrystallized from dichloromethane-diethyl ether.

[Pd(Phpy)(Ph_2**P**(*o*-C_6H_4CH**O**)][CF_3SO_3] (**5**) (yield: 174 mg; 74%). Anal. Calcd for $C_{31}H_{23}F_3NO_4PSPd$ (%): C, 53.2; H, 3.3; N, 2.0. Found: C, 53.0; H, 3.6; N, 2.3. IR Nujol mull ν_{max}, cm^{-1}: 1648(s), 1601(s), 1579(s), 1030(s), 636(m). ^1H NMR (200 MHz; $CDCl_3$) δ_H: 10.38 (1H, d, CHO, $J = 1.8$ Hz); 8.91 (1H, m, arom); 8.62 (1H, dd, $J_{HH} = 8.2$; $J_{Hp} = 4.4$ Hz); 8.04–7.74 (5H, m, arom); 7.63–7.44 (11H, m, arom); 7.23 (1H, m, arom); 7.07 (1H, m, arom); 6.63 (1H, m, arom); 6.33 (1H, m, arom). ^{13}C NMR (50.3 MHz; $CDCl_3$) δ_C: 199.8 (d, CHO, $J_{PC} = 16.6$ Hz); 162.8 (d, Phpy, $J_{PC} = 10.8$ Hz); 148.3 (s, Phpy); 147.0 (d, Phpy, $J_{PC} = 14.8$ Hz); 142.2 (d, O^P ligand, $J_{PC} = 26.0$ Hz); 140.8 (s, O^P ligand); 138.0–119.0 (C_6H_5, C_6H_4, triflate). ^{31}P NMR (121.49 MHz; $CDCl_3$) δ_P: 36.0 (s). ^{19}F NMR (282.4 MHz; $CDCl_3$) δ_F: −77.8 (s). FAB-MS (positive mode) *m/z*: 550 (M^+–CF_3SO_3).

[Pd(Bzq)(Ph_2**P**(*o*-C_6H_4CH**O**)][CF_3SO_3] (**6**) (yield: 140 mg; 62%). Anal. Calcd for $C_{33}H_{23}F_3NO_4PSPd$ (%): C, 54.7; H, 3.2; N, 1.9. Found: C, 54.4; H, 3.0; N, 2.2. IR Nujol

mull ν_{max}, cm^{-1}: 1658(s), 1566(s), 1030(s), 638(m). ^1H NMR (300.13 MHz; $CDCl_3$) δ_H: 10.35 (1H, d, CHO, $J = 1.8$ Hz); 9.10 (1H, m, arom); 8.56 (1H, dd, $J_{HH} = 7.2$; $J_{Hp} = 4.2$ Hz); 8.38 (1H, dd, $J_{HH} = 7.8$; $J_{Hp} = 1.2$ Hz); 7.87 (1H, m, arom); 7.77 (1H, m, arom); 7.71 (2H, m, arom), 7.63 (1H, d, $J_{HH} = 9.0$ Hz); 7.54 (6H, m, arom); 7.49 (1H, d, $J_{HH} = 7.8$ Hz), 7.42 (4H, m, arom), 7.24 (1H, dd, $J_{HH} = 10.8$; $J_{Hp} = 7.8$ Hz); 6.93 (1H, m, arom); 6.39 (1H, m, arom). ^{13}C NMR (75.47 MHz; $CDCl_3$) δ_C: 199.9 (d, CHO, $J_{PC} = 16.2$ Hz); 152.2 (d, Bzq, $J_{PC} = 12.0$ Hz); 146.6 (s, Bzq); 145.9 (s, O^P ligand); 142.7 (d, O^P ligand, $J_{PC} = 30.9$ Hz); 142.1 (s, Bzq); 139.0–122.5 (C_6H_5, C_6H_4, triflate). ^{31}P NMR (121.49 MHz; $CDCl_3$) δ_P: 36.3 (s). ^{19}F NMR (282.4 MHz; $CDCl_3$) δ_F: −77.7 (s). FAB-MS (positive mode) *m/z*: 574 (M^+–CF_3SO_3).

[Pd(Phazo)(Ph_2**P**(*o*-C_6H_4CH**O**)][CF_3SO_3] (**7**) (yield: 191 mg; 85%). Anal. Calcd for $C_{32}H_{24}F_3NO_4PSPd$ (%): C, 52.9; H, 3.3; N, 3.8. Found: C, 53.1; H, 3.3; N, 3.8. IR Nujol mull ν_{max}, cm^{-1}: 1662(s), 1578(s), 1030(s), 636(m). ^1H NMR (200 MHz; $CDCl_3$) δ_H: 10.13 (1H, d, CHO, $J = 2.6$ Hz); 8.65 (1H, dd, $J_{HH} = 4.6$; $J_{Hp} = 4.4$ Hz); 8.06 (1H, dd, $J_{HH} = 7.6$; $J_{Hp} = 1.4$ Hz); 8.00–7.78 (4H, m, arom); 7.54–7.21 (12H, m, arom); 7.76 (3H, m, arom); 6.76 (1H, m, arom); 6.23 (1H, m, arom). ^{13}C NMR (50.3 MHz; $CDCl_3$) δ_C: 199.6 (d, CHO, $J_{PC} = 17.2$ Hz); 164.6 (s, Phazo); 150.1 (d, Phazo, $J_{PC} = 15.2$ Hz); 149.6 (s, O^P ligand); 142.8 (d, O^P ligand, $J_{PC} = 32.0$ Hz); 137.6–123.0 (C_6H_5, C_6H_4, triflate). ^{31}P NMR (121.49 MHz; $CDCl_3$) δ_P: 34.8 (s). ^{19}F NMR (282.4 MHz; $CDCl_3$) δ_F: −77.8 (s). FAB-MS (positive mode) *m/z*: 577 (M^+–CF_3SO_3).

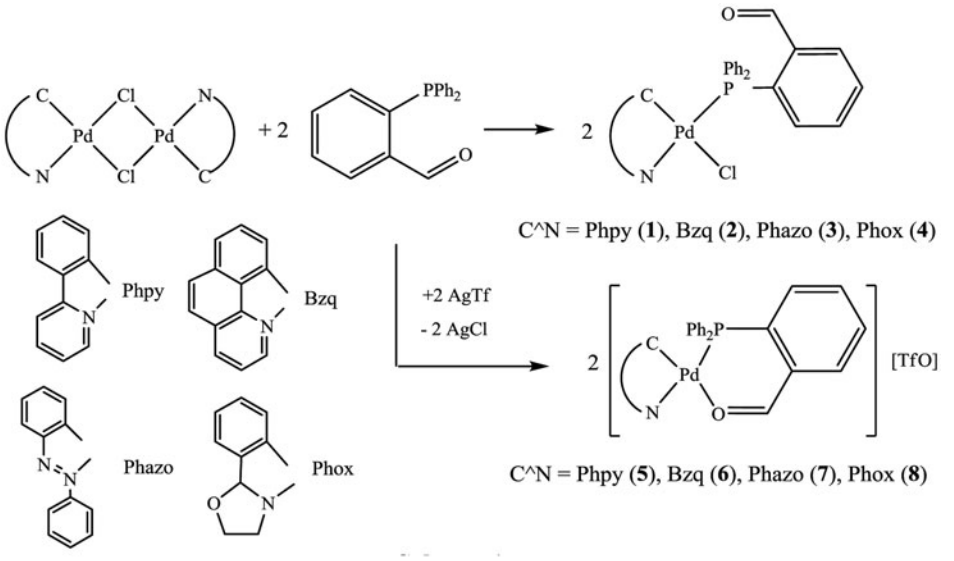
[Pd(Phox)(Ph_2**P**(*o*-C_6H_4CH**O**)][CF_3SO_3] (**8**) (yield: 154 mg; 64%). Anal. Calcd for $C_{29}H_{23}F_3NO_5PSPd$ (%): C, 50.3; H, 3.3; N, 2.0. Found: C, 50.0; H, 3.6; N, 2.2. IR Nujol mull ν_{max}, cm^{-1}: 1632(s), 1578(s), 1564(s), 1028(s), 634(m). ^1H NMR (200 MHz; $CDCl_3$) δ_H: 10.13 (1H, d, CHO, $J = 1.4$ Hz); 8.54 (1H, m, arom); 7.90 (2H, m, arom); 7.68–7.24 (12H, m, arom); 7.03 (1H, m, arom); 6.71 (1H, m, arom); 6.20 (1H, m, arom); 4.86 (2H, t, –CH_2–, $J = 9.4$ Hz); 4.28 (2H, t, –CH_2–, $J = 9.4$ Hz). ^{13}C NMR (50.3 MHz; $CDCl_3$) δ_C: 199.3 (d, CHO, $J_{PC} = 17.0$ Hz); 175.4 (d, Phox, $J_{PC} = 8.8$ Hz); 144.4 (s, Phox); 142.6 (d, O^P ligand, $J_{PC} = 32.0$ Hz); 137.2–117.3 (C_6H_5, C_6H_4, triflate); 71.2 (s, Phox); 49.9 (s, Phox). ^{31}P NMR (121.49 MHz; $CDCl_3$) δ_P: 34.3 (s). ^{19}F NMR (282.4 MHz; $CDCl_3$) δ_F: −77.8 (s). FAB-MS (positive mode) *m/z*: 542 (M^+–CF_3SO_3).

3. Results and discussion

3.1. *Synthesis and spectroscopic characterization*

In dichloromethane, the chloro-bridged cyclometallated dimers [{Pd(μ-Cl)(C^N)}$_2$] react under the conditions described in the experimental section with 2-(diphenylphosphino) benzaldehyde to give moderate to good yields the yellow derivatives **1**–**4** in which the ligand displays η^1-phosphine coordination. The spectroscopic and analytical data support the proposed structures presented in scheme 1.

Infrared spectra of **1**–**4** show characteristic absorptions of the corresponding cyclometallated ligand, together with a ν(CO) absorption in the range observed for free ligand, indicating that the aldehyde oxygen is not coordinated to Pd. A noticeable signal downfield (10.30–10.55 ppm) attributable to the aldehydic proton is found in ^1H-NMR spectra, while the $^{31}P\{^1H\}$-NMR spectra of the mononuclear complexes consist of singlets with chemical shifts in the usual range of Pd(II)-bound phosphorus [26]. Further evidence for the identity of the new complexes comes from FAB mass spectrometry (see experimental). Spectra show a similar pattern of fragmentation which includes the peaks corresponding to [M^+–Cl]. Each peak in the mass spectra actually represents a group of signals resulting



Scheme 1. Preparation of new palladium(II) metal complexes with 2-(diphenylphosphino)benzaldehyde displaying η^1-P (**1-4**) or κ^2-P,O (**5-8**) coordination modes.

from a number of combinations of naturally occurring isotopes. This situation becomes more complex when transition metals are involved, since transition metals have a large number of natural isotopes. Thus, Pd has six isotopes with masses ranging from 101.91 to 109.91, with the most abundant the one with mass 105.90. Comparison of the calculated (with the corresponding formula) and experimental isotopic distribution for the $[M^+–Cl]$ fragments found in the spectra of **1**–**4** is in excellent agreement.

In order to induce a κ^2-P,O coordination mode in 2-(diphenylphosphino)benzaldehyde, the reactions between this ligand and the precursors were performed in the presence of $Ag(CF_3SO_3)$, also in CH_2Cl_2. After elimination of the precipitated AgCl, **5**–**8** were isolated as triflate salts. The presence of $\nu(CF_3SO_3)$ bands in their IR spectra accompanied by a noticeable change in the carbonyl region, with the band now shifted to lower frequencies in comparison with the free ligand and the corresponding P-ligated analogous [20a], confirmed that the proposed reactions took place. ^{19}F-NMR spectra indicated the presence of triflate. Upon chelation, the aldehyde proton resonance shifts upfield as previously reported [20c, 20d, 21]. The ^{31}P chemical shift of cationic complexes is displaced downfield with regard to free ligand but in less than corresponding P-coordinated complexes, as reported previously for Pd(II) [20c, 20d], Cu(I) [27] and Ru(II) [21]. The coordination of aldehyde to palladium is also evidenced by the *ca.* 10 ppm downfield shift of the C=O resonance in ^{13}C spectra of **5**–**8** with regard to **1**–**4**, a fact that has been previously reported [21]. The positive FAB mass spectra of the complexes show the signals at the same *m/z* as **1**–**4** due in this case to the M^+ fragments, indicating $[CF_3SO_3]$ loss.

Throughout the discussion, a regioselective P-trans-N bonding mode is assumed for both P-monodentated and P^O-chelating complexes. For the latter, the structural analysis by X-ray diffraction of **8** confirms the relative *cis* position of the phosphine and the metallated carbon suggested by NMR data and reported in related complexes [20c, 20d, 26c]. This is the typical arrangement of the phosphine in cyclopalladated complexes of the type

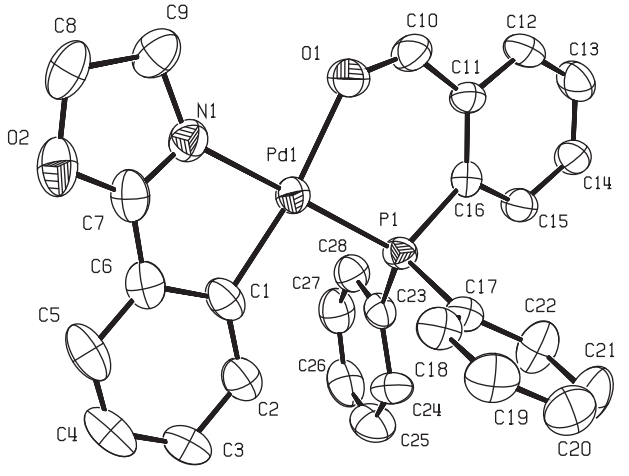


Figure 1. ORTEP diagram of **8** with the atom numbering scheme; displacement ellipsoids are drawn at the 50% probability level.

Table 2. Selected bond lengths (Å) and angles (°) for **8**.

Pd1–C1	2.020(6)
Pd1–N1	2.073(5)
Pd1–O1	2.106(5)
Pd1–P1	2.2453(16)
C1–Pd1–N1	81.6(3)
C1–Pd1–O1	168.8 (2)
C1–Pd1–P1	97.6(2)
N1–Pd1–O1	87.92(19)
N1–Pd1–P1	177.99(14)
O1–Pd1–P1	92.75(13)

[Pd(C^N)(phosphine)(L)] [26 b, d] (L=anionic monodentate ligand), very similar to **1**–**4**, due to the so-called *transphobia* effect [28].

3.2. *Crystal structure of 8*

It was possible to grow single crystals of 8 suitable for X-ray diffraction so its molecular structure was determined and is shown in figure 1, with bond lengths and angles in table 2. The asymmetric part of the unit cell of **8** contains one molecule.

Table 3. Selected bond lengths (Å) and angles (°) corresponding to interactions displayed in figure 2.

Interaction			
Hydrogen-bonding "dimer"		Hydrogen-bonding triflate	
Length	(Å)	Length	(Å)
O2···C8	3.193	O5···H8A	2.609
O2···H8B	2.743	O3···H8B	2.770
O2···H8A	3.119	O3···H9A	2.965
Angle	(°)	Angle	(°)
C8–H8A–O2	85.50	C8–H8A–O5	140.32
C8–H8B–O2	108.99	C8–H8B–O3	131.71
		C9–H9A–O3	125.83

The crystal packing results from several C–H···O hydrogen-bonding interactions that involve three or more centres together with π–π face-to-face interactions. As inferred from data collected in table 3, the hydrogen-bonding interactions can be described as moderate to weak following the classification of Jeffrey who called moderate hydrogen bonds X–H···A when distances X···A and H···A are between 2.5–3.2 and 1.5–2.2 Å, respectively, and the angle X–H–A > 130°. The same author described a weak interaction when the distances are >3.2 Å and > 2.2 Å and the angle is between 130 and 90° [29].

Figure 2 displays the resulting packing, with interactions between two molecules as complementary hydrogen-bonding pairs [30]. Thus, the oxygen of each oxazolinyl

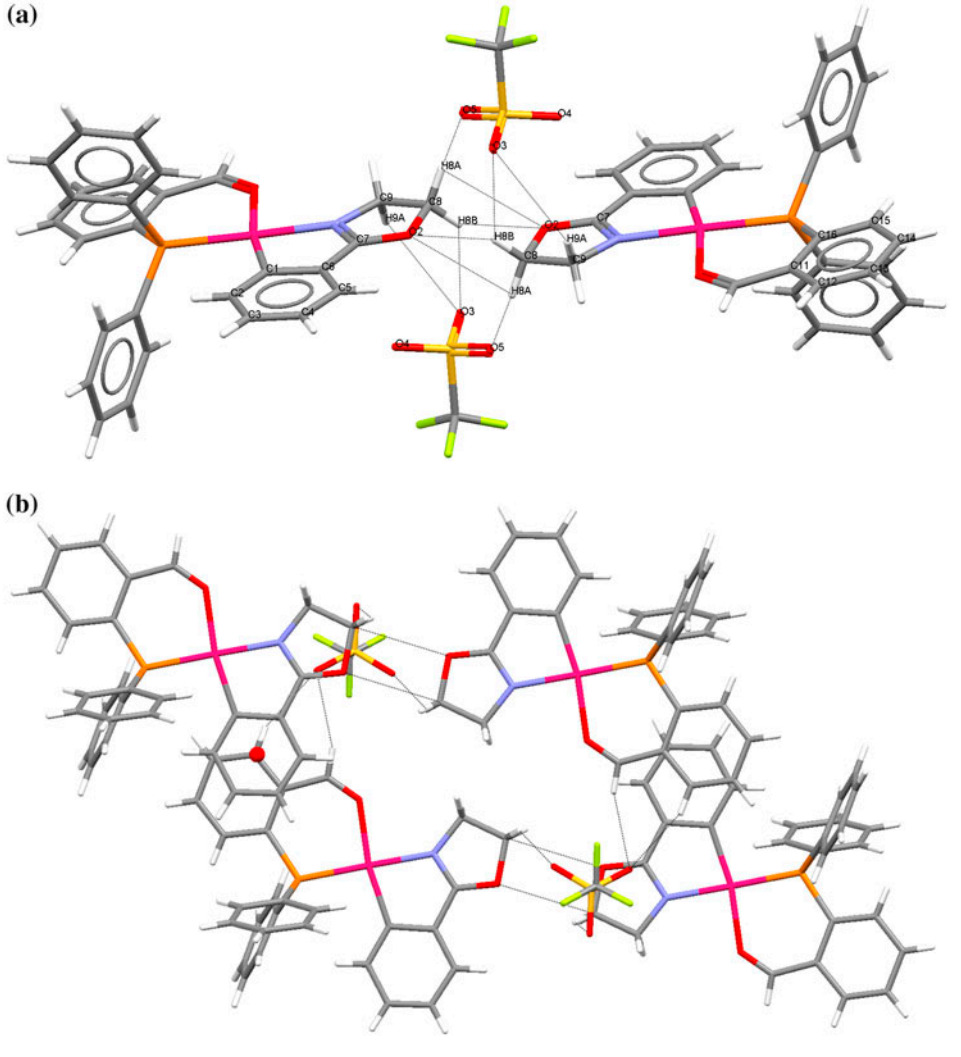


Figure 2. Two views of the crystal packing in **8** highlighting the main interactions. (a) Perspective displaying several C–H···O interactions. Complementary hydrogen-bonding "dimers" are formed by interaction between O2 from one molecule and H8A/H8B of the other. Two triflate anions reinforce this interaction through O3 and O5 oxygens as displayed above. (b) View perpendicular to phenyl (C1–C6) plane to emphasize π–π interactions between two dimers. Some trifaltes have been omitted for clarity.

Table 4. Bond lengths (Å) and angles (°) for **8** and similar complexes [26b].

	8	**4** [30]	**4a** [30]	**5a** [30]
Pd1–C1	2.020(6)	1.976(4)	2.027(3)	2.046(12)
Pd1–N1	2.073(5)	2.017(3)	2.068(3)	2.062(10)
C1–Pd1–N1	81.6(3)	81.08(6)	81.04(12)	81.O(4)

fragment interacts with hydrogens from adjacent methylenic groups of the other molecule. This contact is reinforced by interaction of the oxygens of two triflates that bridge the $-CH_2-$ groups (figure 2(a)). The dimers are completed through π–π face-to-face interactions between phenyl groups of phenyloxazoline and chelating phenyl from 2-(diphenylphosphino)benzaldehyde (red dot centroid [C1–C2–C3–C4–C5–C6]–C12 distances of 3.525 Å), as shown in figure 2(b). We have not found short range interactions involving fluorines of triflate anions.

The structure around palladium may be described as nearly planar and deviation from planar coordination has been quantified by measures of improper torsion angles: 1.36 and −2.75° (square pyramidal) [31]. The angle between planes C1–Pd1–N1 and O1–Pd1–P1 is 4.50(15)°. The distances Pd1–C1/Pd1–N1 and the angle C1–Pd1–N1 in the orthometallated moiety are similar to those found in mononuclear complexes containing the same ligand [26b]. Distances and angles are listed in table 4.

The 2-(diphenylphosphino)benzaldehyde fragment displays very close Pd1–P1 and Pd1–O1 distances to the ones found in the few crystals reported to date containing the chelated ligand [20a, 20d], 2.2453(16) Å *versus* 2.2508(10) and 2.237(1) Å; 2.106(5) Å *versus* 2.106(2) and 2.106(4) Å, respectively, with a larger bite angle O1–Pd1–P1 of 92.75 (13)° (88.16(6) and 90.5(1)°). As expected also a similar C=O distance, C10–O1 = 1.217 (7) Å *versus* 1.219(4) and 1.211(6) Å, indicative of an important double-bond character has been found.

Methods for conformational classification of medium size rings have been described [32]. Using the classification method, the five- Pd1–N1–C7–C6–C1 and six-Pd1–O1–C10–C11–C16–P1 membered palladacycles exhibit almost planar conformation for $\sigma = 10°$ (HC = 0.5143; $E = 0.4857$ and SB = 0.9876; HC = 0.0100; $E = 0.0024$, respectively). The six-membered ring of our compound detailed above can be described as *screw-boat* deformed 27°, while a comparison with related structures labeled with refcodes UZEBEH (SB = 0.9387; $E = 0.0441$; HC = 0.0172) [20a] and YIKTOC (SB = 0.9947; HC = 0.0049; $E = 0.0004$) [20d] shows that they are also *screw-boats* deformed 16 and 14°, respectively.

4. Conclusion

The versatile coordination properties of 2-(diphenylphosphino)benzaldehyde $Ph_2P(o\text{-}C_6H_4CHO)$ have been stated by synthesizing and characterizing two series of cyclometallated palladium(II) complexes in which P-monodentate or P,O-bidentate coordination modes are displayed. NMR spectroscopy is a crucial tool to identify the proposed coordination modes. Despite the wide use of 2-(diphenylphosphino)benzaldehyde as precursor in the preparation of iminophosphine ligands, its coordination chemistry remains largely unexplored. The fact that related mononuclear cyclopalladated complexes have found interesting catalytic applications [33] allows us to envisage future studies on the compounds presented here. The crystal structure of one of the new complexes has been determined,

confirming the proposed formula and providing an interesting structural discussion regarding its crystal packing and conformational trends.

Acknowledgements

We thank Fundación Séneca (project 08670/PI/08) for partial financial support. Carmen Ruiz Padilla is gratefully acknowledged for her contribution to initial stages of this work.

References

[1] A. Bader, E. Lindner. *Coord. Chem. Rev.*, **108**, 27 (1991).
[2] G.R. Newkome. *Chem. Rev.*, **93**, 2067 (1993).
[3] C.S. Slone, D.A. Weinberger, C.A. Mirkin. *Prog. Inorg. Chem.*, **48**, 233 (1999).
[4] P. Braustein, F. Naud. *Angew. Chem. Int. Ed.*, **40**, 680 (2001) and references therein.
[5] P. Braustein. *J. Organomet. Chem.*, **689**, 3953 (2004) and references therein.
[6] G.M. Kapteijn, M.P.R. Spee, D.M. Grove, H. Kooijman, A.L. Spek, G. van Koten. *Organometallics*, **15**, 1405 (1996).
[7] P. Braunstein, C. Frison, X. Morise, R.A. Adams. *J. Chem. Soc., Dalton Trans.*, 2205 (2000).
[8] C. Fliedel, G. Schnee, P. Braunstein. *Dalton Trans.*, 2474 (2009).
[9] C.W. Machan, A.M. Spokoyny, M.R. Jones, A.A. Sarjeant, C.L. Stern, C.A. Mirkin. *J. Am. Chem. Soc.*, **133**, 3023 (2011).
[10] (a) Z.G. Specht, S.A. Cortes-Llamas, H.N. Tran, C.J. van Niekerk, K.T. Rancudo, J.A. Golen, C.E. Moore, E. Curtis, A.L. Rheingold, T.J. Dwyer, D.B. Grotjahn. *Chem. Eur. J.*, **17**, 6606 (2011); (b) F. Guyon, M. Knorr, A. Garillon, C. Strohmann. *Eur. J. Inorg. Chem.*, 282 (2012); (c) L. Canovese, F. Visentin, C. Levi, C. Santo, V. Bertolasi. *Inorg. Chim. Acta*, **390**, 105 (2012) *Inorg. Chim. Acta*.
[11] (a) M.S. Rosen, A.M. Spokoyny, C.W. Machan, C. Stern, A. Sarjeant, C.A. Mirkin. *Inorg. Chem.*, **50**, 1411 (2011) and references therein; (b) C.W. Tate, A. deMello, A.D. Gee, S. Kealey, R. Vilar, A.J.P. White, N.J. Long. *Dalton Trans.*, 83 (2012).
[12] C.W. Rogers, M.O. Wolf. *Coord. Chem. Rev.*, **233–234**, 341 (2002).
[13] W.-H. Zhang, S.W. Chien, T.S. Andy Hor. *Coord. Chem. Rev.*, **255**, 1991 (2011).
[14] (a) A. Scrivanti, U. Matteoli, V. Beghetto, S. Antonaroli, B. Crociani. *Tetrahedron*, **58**, 6881 (2002) and references therein; (b) S. Doherty, J.G. Knight, T.H. Scanlan, M.R.J. Elsegood, W. Clegg. *J. Organomet. Chem.*, **650**, 231 (2002); (c) T. Schultz, N. Schmees, A. Pfaltz. *Appl. Organomet. Chem.*, **18**, 595 (2004); (d) B. Crociani, S. Antonaroli, A. Marini, U. Matteoli, A. Scrivanti. *Dalton Trans.*, 2698 (2006); (e) B.C.E. Makhubela, A. Jardine, G.S. Smith. *Appl. Catal., A*, **393**, 231 (2011).
[15] (a) C.A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini, G. Scapacci. *J. Chem. Soc., Dalton Trans.*, 3371 (1992); (b) J.R. Dilworth, S.D. Howe, A.J. Hutson, J.R. Miller, J. Silver, R.M. Thomson, M. Harman, M.B. Hursthouse. *J. Chem. Soc., Dalton Trans.*, 3553 (1994); (c) L. Crociani, G. Bandoli, A. Dolmella, M. Basato, B. Corain. *Eur. J. Inorg. Chem.*, 1811 (1998).
[16] G. Sánchez, J.L. Serrano, M.A. Moral, J. Pérez, E. Molins, G. López. *Polyhedron*, **18**, 3057 (1999).
[17] (a) G. Sánchez, J.L. Serrano, F. Ruiz, G. López. *J. Fluorine Chem.*, **91**, 165 (1998); (b) G. Sánchez, J.L. Serrano, F. Momblona, F. Ruiz, J. García, J. Pérez, G. López, P.A. Chaloner, P. Hitchcock. *Polyhedron*, **20**, 571 (2001).
[18] (a) G. Sánchez, J. García, J.L. Serrano, L. García, J. Pérez, G. López. *Inorg. Chim. Acta*, **363**, 1084 (2010); (b) G. Sánchez, F. Momblona, J. García, J.L. Serrano, L. García, E. Pérez, J. Pérez, G. López. *J. Coord. Chem.*, **55**, 917 (2002).
[19] (a) C. Ntoras, P.J. Cox, P. Aslanidis. *Polyhedron*, **34**, 171 (2012) and references therein; (b) E.W. Ainscough, A.M. Brodie, S.L. Ingham, J.M. Waters. *Inorg. Chim. Acta*, **234**, 163 (1995); (c) R. El Mail, M.A. Garralda, R. Hernández, L. Ibarlucea. *J. Organomet. Chem.*, **648**, 149 (2002); (d) X. Chen, F.J. Femia, J.W. Babich, J. Zubieta. *Inorg. Chim. Acta*, **315**, 147 (2001); (e) W.-Y. Yeh, C.-S. Lin, P.-M. Peng, G.-H. Lee. *Organometallics*, **23**, 917 (2004); (f) R. El Mail, M.A. Garralda, R. Hernández, L. Ibarlucea. *Organometallics*, **19**, 5310 (2000); (g) M.A. Garralda, R. Hernandez, L. Ibarlucea, E. Pinilla, M.R. Torres. *Organometallics*, **22**, 3600 (2003).
[20] (a) C.S. Chen, H.F. Dai, C.H. Chen, W.Y. Yeh. *Inorg. Chim. Acta*, **376**, 396 (2011); (b) N.J.S. Costa, P.K. Kiyohara, A.L. Monteiro, Y. Coppel, K. Philippot, L.M. Rossi. *J. Catal.*, **276**, 382 (2010); (c) R. Ares, D. Vazquez-Garcia, M. Lopez-Torres, A. Fernandez, N. Gomez-Blanco, J.M. Vila, J.J. Fernandez. *J. Organomet. Chem.*, **693**, 3655 (2008); (d) R. Ares, M. Lopez-Torres, A. Fernandez, D. Vazquez-Garcia, M.T. Pereira, J.M. Vila, L. Naya, J.J. Fernandez. *J. Organomet. Chem.*, **692**, 4197 (2007); (e) H. Mahalakshmi, P.P. Phadnis, V.K. Jain, E.R.T. Tiekink. *Indian J. Chem., Sect. A*, **43**, 2287 (2004).

[21] P. Crochet, M.A. Fernández-Zumel, C. Beauquis, J. Gimeno. *Inorg. Chim. Acta*, **356**, 114 (2003).
[22] (a) A.C. Cope, R.W. Siekman. *J. Am. Chem. Soc.*, **87**, 3273 (1965); (b) A. Kasahara. *Bull. Chem. Soc. Jpn.*, **41**, 1272 (1968); (c) E.C. Constable, A.M.W. Cargill Thompson, T.A. Leese, D.G.F. Reese, D.A. Tocher. *Inorg. Chim. Acta*, **182**, 93 (1991); (d) I.P. Smoliakova, K.J. Keuseman, D.C. Haagenson, D.M. Wellmann, P.B. Colligan, N.A. Kataeva, A.V. Churakov, L.G. Kuz'mina, V.V. Dunina. *J. Organomet. Chem.*, **603**, 86 (2000).
[23] Nonius (1999). *COLLECT*. Nonius BV, Delft, the Netherlands.
[24] Denzo-Scalepack, Z. Otwinowski, and W. Minor. In *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods in Enzymology, Volume 276: Macromolecular Crystallography, Part A*, C.W. Carter, Jr. and R.M. Sweet (Eds.), pp. 307–326, Academic Press, New York (1997).
[25] G.M. Sheldrick. *SHELX-97 Programs for Crystal Structure Analysis* (*Release 97–2*), University of Göttingen, Göttingen (1998).
[26] (a) J.L. Serrano, L. García, J. Pérez, E. Pérez, G. Sánchez, J. García, P. Sehnal, S. De Ornellas, T.J. Williams, I.J.S. Fairlamb. *Organometallics*, **30**, 5095 (2011); (b) J.L. Serrano, L. García, J. Pérez, E. Pérez, J. García, G. Sánchez, G. López, I.J.S. Fairlamb, M. Liu. *Polyhedron*, **27**, 1699 (2008); (c) G. Sánchez, J. García, D. Meseguer, J.L. Serrano, L. García, J. Pérez, G. López. *J. Chem. Soc., Dalton Trans.*, 4709 (2003) and references therein; (d) J.L. Serrano, L. García, J. Pérez, E. Pérez, J. Vives, G. Sánchez, G. López, E. Molins, A.G. Orpen. *Polyhedron*, **21**, 1589 (2002).
[27] W.-Y. Yeh, Y.-C. Liu, P.-M. Peng, G.-H. Lee. *Inorg. Chim. Acta*, **358**, 1987 (2005).
[28] (a) J. Vicente, A. Arcas, D. Bautista, P.G. Jones. *Organometallics*, **16**, 2127 (1997); (b) J. Vicente, J.A. Abad, A.D. Frankland, M.C. Ramírez de Arellano. *Chem. Eur. J.*, **5**, 3066 (1999).
[29] (a) J.W. Steed, J.L. Atwood. *Supramolecular Chemistry*, 2nd edn, pp. 449–452, John Wiley, Chichester (2009); (b) C. Laurence, M. Berthelot. *Perspect. Drug Discovery Des.*, **18**, 39 (2000); (c) T. Steiner. *Angew. Chem. Int. Ed.*, **41**, 48 (2002); (c) G.A. Jeffrey. *An Introduction to Hydrogen Bonding,* Oxford University Press, Oxford (1997).
[30] (a) Z. Qin, M.C. Jennins, R.J. Puddephatt. *Inorg. Chem.*, **40**, 6220 (2001); (b) G.R. Desiraju. *Angew. Chem. Int. Ed. Engl.*, **34**, 2311 (1995).
[31] J. Pérez, L. García, E. Pérez, J.L. Serrano, J.F. Martínez, G. Sánchez, G. López, A. Espinosa, M. Liu, F. Sanz. *New J. Chem.*, **27**, 1490 (2003).
[32] J. Pérez, K. Nolsøe, M. Kessler, L. García, E. Pérez, J.L. Serrano. *Acta Cryst.* **B61**, 585 (2005).
[33] S.J. Sabounchei, M. Ahmadi, Z. Nasri. *J. Coord. Chem.*, **66**, 411 (2013).