Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Organometallic Chemistry 691 (2006) 2891–2901
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis, characterization and solid state structures of thiosemicarbazone palladacycles: Influence of hydrogen bonding in the molecular arrangement

Javier Martínez [a], Luis A. Adrio [a], José M. Antelo [a], Juan M. Ortigueira [a], M[a] Teresa Pereira [a], Margarita López-Torres [b], José M. Vila [a,*]

[a] Departamento de Química Inorgánica, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain
[b] Departamento de Química Fundamental, Universidad de A Coruña, 15071 A Coruña, Spain

Received 11 December 2005; received in revised form 21 February 2006; accepted 22 February 2006
Available online 28 February 2006

Abstract

Treatment of the thiosemicarbazones 4-$FC_6H_4C(Me)$=NN(H)C(=S)NHR, (R = Me, **a**; Ph, **b**) and 2-$ClC_6H_4C(Me)$=NN(H)C(=S)NHR (R = Ph, **c**) with lithium tetrachloropalladate(II) in methanol or palladium(II) acetate in acetic acid gave the tetranuclear cyclometallated complex $[Pd\{4\text{-}FC_6H_3C(Me)=NN=C(S)NHR\}]_4$ (**1a**, **1b**) and $[Pd\{2\text{-}ClC_6H_3C(Me)=NN=C(S)NHPh\}]_4$ (**1c**). Reaction of these tetramers with the diphosphines dppe, t-dppe, dppp or dppb in a 1:2 molar ratio gave the dinuclear cyclometallated complexes $[(Pd\{4\text{-}FC_6H_3C(Me)=NN=C(S)NHR\})_2(\mu\text{-}Ph_2P(CH_2)_nPPh_2)]$, ($n = 2$, **2a**, **2b**; 3, **4a**, **4b**; 4, **5a**, **5b**), $[(Pd\{4\text{-}FC_6H_3C(Me)=NN=C(S)NHPh\})_2(\mu\text{-}Ph_2PCH=CHPPh_2)]$, (**3a**, **3b**) and $[(Pd\{2\text{-}ClC_6H_3C(Me)=NN=C(S)NHR\})_2(\mu\text{-}Ph_2P(CH_2)_nPPh_2)]$, ($n = 2$, **2c**, **2d**; 3, **4c**, **4d**; 4, **5c**, **5d**), $[(Pd\{2\text{-}ClC_6H_3C(Me)=NN=C(S)NHPh\})_2(\mu\text{-}PPh_2CH=CHPPh_2)]$, (**3c**, **3d**). The X-ray crystal structure of the ligand **b** and the complexes **3c**, **4a** and **4d** were determined. The structures of complexes **4a** and **4d** show that the different disposition of the chain cyclometallated of the thiosemicarbazones (in the same orientation or in the opposite one) is due to the different H bonds produced.

Keywords: Cyclometallated; Thiosemicarbazones; Palladium; C–H activation; H bonds

1. Introduction

Palladium cyclometallated compounds comprise a group of chemicals of great interest within organometallic chemistry, as is inferred from the number of publications devoted to this subject [1–6]. Particular attention has been drawn to their applications as catalysts in organic synthesis, in insertion and regio- and stereo-selective reactions and as catalysts in organic synthesis [7–15], as well as to the mechanistic aspects [16,17]. Thus, there is a continuing quest for new cyclometallated species with different types of ligands bearing N, P, O and/or S donor atoms. Compounds containing two non-carbon donor atoms are known to act as tridentate ligands for palladium(II) or platinum(II) and can produce cyclometallated complexes having two fused rings at the metal centre [18–28]; a particular case being thiosemicarbazone and semicarbazone ligands [23–25] which may bind to the metal atom as terdentate [C, N, S] and [C, N, O], respectively. Two unique features distinguish thiosemicarbazones form other terdentate [C, N, X] (X = N, O, P) ligands: (a) the strength of the $Pd–S_{chelating}$ bond, which hinders opening of the metallated and coordination rings at the metal center, thus making the ligands excellent pincer species which powerfully secure three of the four coordination positions of the metal, allowing only the fourth coordination site to undergo further reaction with nucleophiles; (b) metallation of the ligand

* Corresponding author. Fax: +34 981595012.
E-mail address: qideport@usc.es (J.M. Vila).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.02.030

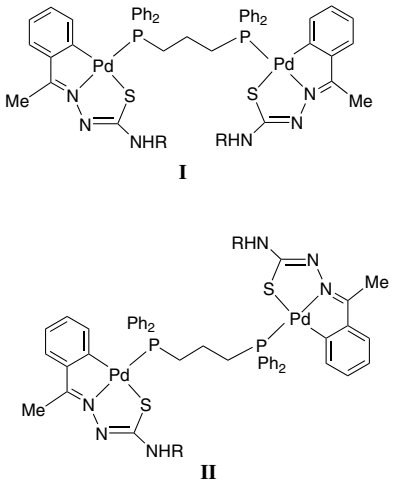


Fig. 1. *cisoid* (I) and *transoid* (II) geometries for the dinuclear compounds.

yields tetrameric compounds bearing a central Pd_4S_4 central core. Upon reaction of the tetranuclear species with tertiary diphosphines, compounds with bridging or with mono-coordinate diphophine are obtained, the strength of the Pd–$S_{chelating}$ bond preventing the chelating bidentate mode of the diphosphine ligand [23,24]; with η^1-diphosphines the corresponding compounds may behave as bidentate $[P,S]$ metalloligands as we have previously shown [29]. In the cases with bridging diphosphines the ^{1}H and ^{31}P NMR data suggest symmetrical arrangements across the phosphine ligand, the *transoid* geometry being preferred to the *cisoid* one, as steric effects are minimized, as solid structural analysis has shown [24,30] (Fig. 1).

However, the *cisoid* geometry may appear if intermolecular hydrogen bonding is present as is herein reported.

2. Results and discussion

The ligands **a**–**c** were prepared by reaction of 4-methyl or 4-phenyl-3-thiosemicarbazide with 4′-fluoro- or 2′-chloro acetophenone as appropriate, in good yields (see Section 3). The NHR and NH groups gave rise to characteristic υ(N–H) bands in the IR spectra ca. 3300 and 3200 cm^{-1}, respectively, the latter disappears in the spectra of the complexes [31]; the typical υ(C=N) and υ(C=S) stretches appeared in the ranges 1620–1590 and 840–800 cm^{-1}, respectively. The ^{1}H NMR spectra showed signals ca. δ 8.64 (**a**), δ 9.35 (**b**), δ 9.34 (**c**) and δ 7.59 (**a**), δ 7.53 (**b**), δ 7.43 (**c**) for the NHR and NH protons, respectively. From the ligands synthesis of the compounds was achieved y anyone of the three alternative methods described, i.e., (a) potassium tetrachloropalladate in ethanol; (b) lithium tetrachloropalladate in methanol; (or) palladium(II) acetate in glacial acetic acid, resulting in all cases tetranuclear species, [Pd{4-FC_6H_3C(Me)=NN=C(S)NHR}]$_4$ (**1a**, **1b**) and [Pd{2-ClC_6H_3C(Me)=NN=C(S)–NHPh}]$_4$ (**1c**), as air-stable solids, with the ligand in the E,Z configuration, which were fully characterized by microanalytical, mass spectra, IR and ^{1}H and ^{31}P–{^{1}H} NMR determinations (see Section 3). The mass spectrum (FAB) showed peaks at m/z 1319 (**1a**), 1568 (**1b**) and 1634 (**1c**) for the molecular ion whose isotopic composition suggests a tetranuclear complex of formula $C_{40}H_{40}F_4N_{12}Pd_4S_4$ (**1a**), $C_{60}H_{48}F_4N_{12}Pd_4S_4$ (**1b**) and $C_{60}H_{40}Cl_4N_{12}Pd_4S_4$ (**1c**) (see Section 3; Scheme 1).

The υ(C=N) band was shifted to lower wavenumbers ca. 30–40 cm^{-1} [32] indicating palladium coordination to the C=N moiety at the nitrogen lone pair [33,34]. Absence of the N*H* resonance in the ^{1}H NMR spectra indicated deprotonation of the –NH– group [35,36], which causes loss of the C=S double bond character as confirmed by the non-existence of the υ(C=S) band.

For complexes **1a**, **1b** metallation of the ligands was clear from the absence of the AA′XX′ spin system of the *para*-substituted phenyl ring; in its place an uncomplicated first order three-spin system was obtained, where coupling to the ^{19}F nucleus was observed. For **1d** the complex ABCD spin system in the ligand gave rise to three proton resonances which were unambiguously assigned (see Section 3).

2.1. Reactivity of the complexes

Treatment of **1a**–**1c** with the corresponding diphosphine in a 1:2 molar ratio produced compounds [{Pd[4-FC_6H_3C(Me)=NN=C(S)NHR]}$_2$(μ-$Ph_2P(CH_2)_nPPh_2$)] ($n=2$, R = Me, **2a**, R = Ph, **2b**; $n=3$, R = Me, **4a**, R = Ph, **4b**; $n=4$, R = Me, **5a**, R = Ph, **5b**) [{Pd[4-FC_6H_3C(Me)=NN=C(S)NHR]}$_2$(μ-Ph_2PCH=$CHPPh_2$)] (R = Me, **3a**, R = Ph, **3b**) [{Pd[2-ClC_6H_3C(Me)=NN=C(S)NHPh]}$_2$(μ-$Ph_2P(CH_2)_nPPh_2$)] ($n=2$, **2c**; $n=3$, **4c**; $n=4$, **5c**) [{Pd[2-ClC_6H_3C(Me)=NN=C(S)NHPh]}$_2$-(μ-Ph_2PCH=$CHPPh_2$)] (**3c**) as pure air-stable solids, which were completely characterised (see Section 3).

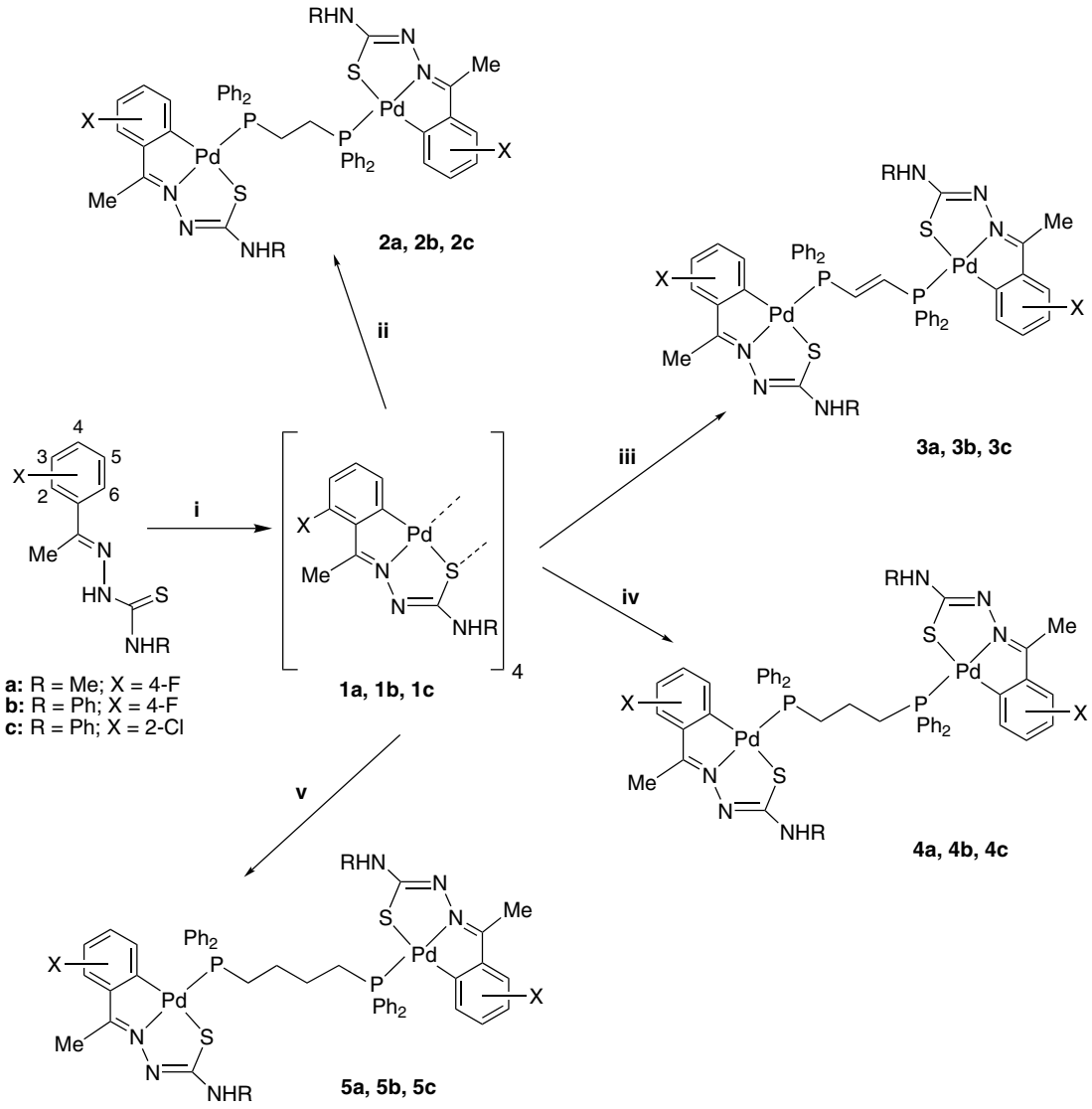
The ^{1}H NMR spectra showed the high field shift of the H5 resonance by ca. 1–1.5 ppm, which was coupled to the ^{31}P nucleus, pointing towards a P *trans* to N arrangement [37]. The symmetric nature of the complexes was put forward by the ^{1}H NMR spectra, which showed only one set of signals; and accordingly, a singlet was observed for the ^{31}P resonance due to two equivalent phosphorus nuclei; the chemical shift value for the latter also supported a phosphorus *trans* to nitrogen geometry [38–40].

2.2. Structural studies: crystal structures of ligand *b* and of complexes *4a* and *4c*

Suitable crystals were grown by slowly evaporating chloroform/*n*-hexane solutions. The crystal structures are shown in Figs. 2, 4 and 5. Crystal data are given in Table 1.

2.2.1. 4-FC_6H_4C(Me)=NN(H)C(=S)NHMe (*b*)

Ligand **b** crystallizes in the monoclinic $P21/n$ space group as the E,Z-isomer relative to the N(1)–C(7) and N(8)–C(3) bonds, respectively, Fig. 2.



Scheme 1. (i) $K_2[PdCl_4]$/EtOH; $Li_2[PdCl_4]$/MeOH; $Pd(AcO)_2$/AcOH; (ii) $Ph_2P(CH_2)_2PPh_2$/acetone; (iii) *trans*-$Ph_2PCH{=}CHPPh_2$/acetone; (iv) $Ph_2P(CH_2)_3PPh_2$/ acetone; (v) 2: $Ph_2P(CH_2)_4PPh_2$/acetone.

This is typical of thiosemicarbazones where weak N(3)–H(3)...N(1) hydrogen bonding is present (Fig. 2). The C(8)–S(1) and N(1)–C(7) bond distances, 1.6751(18) and 1.286(2) Å, respectively, are consistent with double bond character, as are the C(1)–C(7)–N(1) 115.03(16)° and C(7)–N(1)–N(2) 119.63(15)° bond angles in accordance with sp^2 hybridization of the carbon and nitrogen atoms of the C=N group. The thioamide chain C(1)–C(7)–N(1)–N(2)–C(8)–N(3)–C(9) is planar (rms = 0.0314) and at an angle of 39.4(4)° with the fluorinated phenyl ring (rms = 0.0015). An intermolecular self-assembly between the ligands is established through hydrogen bonds by the MeC=N methyl group, the sulfur atoms and the amido hydrogen atoms. The parameters for the hydrogen bonding interaction (Fig. 3) in ligand **b** are as follows: H(2)...S(1A) 2.844 Å, N(2)...S(1A) 3.701 Å, N(2)–H(2)...S(1A) 174.53°, H(3)...N(1) 2.144 Å, N(3)...N(1) 2.572(3) Å, N(3)–H(3)...N(1) 110.37°, H(15)...S(1A) 2.76 Å, C(15)...S(1A) 3.521(4) Å, C(15)–H(15)...S(1A) 137.01°.

*2.2.2. [(Pd{4-FC$_6$H$_3$C(Me)=NN=C(S)NHMe}$_2$-(μ-Ph$_2$P(CH$_2$)$_3$PPh$_2$)] (**4a**), [(Pd{2-ClC$_6$H$_3$C(Me)=NN=C(S)NHPh}$_2$(μ-Ph$_2$P(CH$_2$)$_3$PPh$_2$)] (**4c**)*

The crystals consist of discrete molecules, separated by normal van der Waals distances. The palladium(II) atoms, which in the case of compound **4a** are not symmetry related (only data for the Pd(1) part will be discussed; those for Pd(2) are very similar and may be obtained from the supplementary information), are bonded to four different donor atoms, a terdentate *C*, *N*, *S* thiosemicarbazone through the aryl C(6) carbon, the imine N(1) nitrogen, and the thioamide S(1) sulfur atom, and to a phosphorus atom P(1) of the bridging diphosphine ligand, in a slightly distorted square-planar coordination, [Pd(1), N(1), S(1),

Table 1
Crystal data and structure refinement data for **b**, **4a** and **4c**

Compound	**b**	**4a**	**4c**
Empirical formula	$C_{15}H_{14}FN_3S$	$C_{50}H_{49}Cl_9F_2N_6\ P_2Pd_2S_2$	$C_{59}H_{52}Cl_8N_6P_2Pd_2S_2$
Formula weight	287.35	1429.86	1467.53
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	1.54184	0.71069	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P21/n$	$P\bar{1}$	$C2/c$
Unit cell dimensions			
a (Å)	14.7389(11)	12.612(5)	33.954(9)
b (Å)	5.8895(3)	15.127(5)	9.062(2)
c (Å)	16.8900(19)	15.855(5)	20.140(5)
α (°)		80.842(5)	
β (°)	100.534(6)	84.603(5)	97.879(5)
γ (°)		81.827(5)	
Volume (Å^3)	1441.4(2)	2948.1(18)	6138(3)
Z	4	2	4
Density (calculated) (Mg/m^3)	1.324	1.611	1.588
Absorption coefficient (mm^{-1})	2.038	1.189	1.098
$F(000)$	600	1432	2952
Crystal size (mm^3)	$0.64 \times 0.08 \times 0.08$	$0.22 \times 0.21 \times 0.07$	$0.24 \times 0.18 \times 0.12$
θ Range for data collection (°)	3.66–73.37	1.30–26.43	1.21–26.43
Index ranges	$0/h/18$, $-7/k/0$, $-20/l/20$	$-15/h/15$, $-18/k/18$, $0/l/19$	$-42/h/42$, $0/k/11$, $0/l/25$
Reflections collected	3026	33653	18508
Independent reflections [R(int)]	2910 [0.0204]	12020 [0.0641]	6224 [0.0809]
Completeness to θ	100.0%	99.1%	98.5%
Absorption correction	Semi-empiric	Semi-empiric	Semi-empiric
Maximum and minimum transmission	0.8539 and 0.3554	0.9214 and 0.7798	0.8795 and 0.7785
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2910/0/183	12020/9/664	6224/0/358
Goodness-of-fit on F^2	1.084	0.998	1.008
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0407$, $wR_2 = 0.1197$	$R_1 = 0.0658$, $wR_2 = 0.1789$	$R_1 = 0.0676$, $wR_2 = 0.1640$
R indices (all data)	$R_1 = 0.0535$, $wR_2 = 0.1271$	$R_1 = 0.1402$, $wR_2 = 0.1983$	$R_1 = 0.1564$, $wR_2 = 0.2127$
Largest difference in peak and hole (e Å^{-3})	0.234 and −0.228	1.496 and −1.337	0.913 and −1.596

C(6), P(1), plane 1] (rms = 0.0052 Å) **4a**, (Fig. 4), [Pd(1), N(1), S(1), C(1), P(1), plane 1] (rms = 0.0585 Å) **4c**, (Fig. 5).

The main difference between the structures is the relative disposition of the cyclometallated moieties, which in compound **4a** adopt a *cisoid* arrangement (Fig. 6), whereas in compound **4c** they appear in a *transoid* fashion (Fig. 7), as a consequence of hydrogen bond formation: in **4a** an *intermolecular* self-assembly between the cyclometallated groups is established through two hydrogen bonds by the sulfur atoms and the amido hydrogen atoms; whereas in **4c** the hydrogen bonds are between the sulfur atoms and the central carbon atom of the bridging diphosphine ligand. In **4a** the hydrogen bonding parameters are H(3)...S(1A) 2.770 Å, N(3)...S(1A) 3.5838 Å, N(3)–H(3)...S(1A) 158.50°, and in **4c** the parameters are H(17)...S(1A) 2.778 Å, C(17)...S(1A) 3.5278 Å, C(17)–H(17)...S(1A) 133.65°, precluding a *cisoid* geometry in this case.

As for the bond distances, and for the angles at palladium, the data observed for both structures are similar and follow essentially analogous alterations from the theoretical values. Thus, the angles between adjacent atoms in the coordination sphere of the palladium centers undergo distorsions from the theoretical value of 90°, consequent upon formation of the two five-membered rings at the metal, and are decreased by ca. 7–10° for the C(6)–Pd(1)–N(1) and C(43)–Pd(2)–N(4) angles, and increased by a similar amount for the C(6)–Pd(1)–P(1) and C(43)–Pd(2)–P(2) angles. All bond distances are within the expected range, with lengthening of the Pd–N bond due to the *trans* influence of the phosphine ligand, which is reflected in the Pd(1)–N(1), 2.039(6) Å **4a** and 2.020(7) Å, **4c**, distances (cf. sum of the covalent radii for palladium and nitrogen, 2.01 Å [41]), and shortening of the Pd–C bond with to the expected value of 2.081 Å [41], as has been observed before [42,43], Pd(1)–C(6) 2.044(8) Å **4a** and 2.040(10) Å **4c**. The S(1)–C(8) 1.769(8) Å **4a**, 1.743(10) Å, **4c**, bond lengths, and the N(2)–C(8), 1.303(10) Å **4a**, 1.319(11) Å, **4c**, lengths, are consistent with increased single and double bond character, respectively, as a result of deprotonation. The planes at palladium: the coordination plane [Pd(1), N(1), S(1), C(6), P(1), plane 1], the metallacycle [Pd(1), C(1), C(6), C(7), N(1), plane 2], the coordination ring [Pd(1), N(1), N(2), C(8), S(1), plane 3] and the metallated phenyl ring [C(1), C(2), C(3), C(4), C(5), C(6), plane 4], are nearly coplanar (angles between planes: 1/2 = 1.10(0.08), 1/3 = 0.56(0.04), 1/4 = 4.10(0.13), 2/3 = 1.10 (0.09), 2/4 = 3.04(0.14), 3/4 = 4.13(0.13)° **4a**; 1/2 = 4.45 (0.18), 1/3 = 5.06(0.11), 1/4 = 6.57(0.22), 2/3 = 4.72(0.16), 2/4 = 2.27(0.25), 3/4 = 6.58(0.24)° **4c**). As for the overall

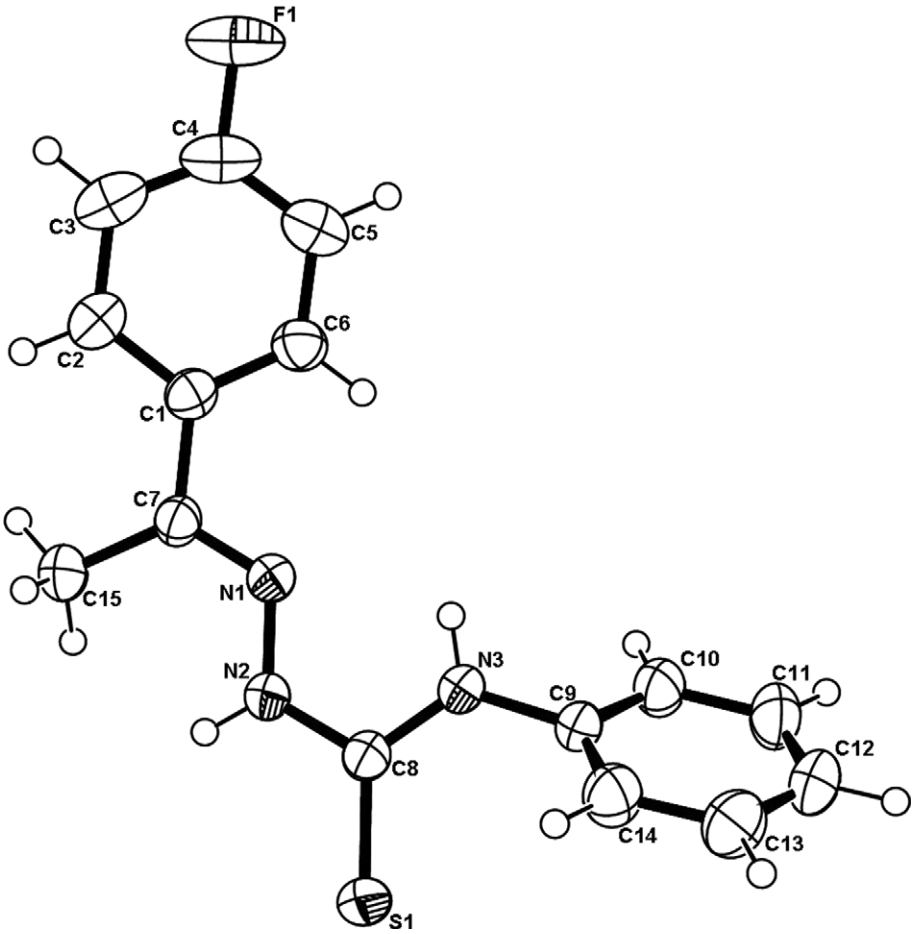


Fig. 2. An ORTEP drawing of the molecular structure for **b** with labeling scheme (50% probability). Selected bond lengths and angles: C(1)–C(7) 1.484(2); N(1)–C(7) 1.286(2); N(1)–N(2) 1.374(2); N(2)–C(8) 1.362(2); S(1)–C(8) 1.6751(18); C(8)–N(3) 1.341(2); C(6)–C(1)–C(7) 120.32(16); N(1)–C(7)–C(1) 115.03(16); C(7)–N(1)–N(2) 119.63(15); C(8)–N(2)–N(1) 118.20(14); N(3)–C(8)–N(2) 114.56(16); N(3)–C(8)–S(1) 125.58(13); N(2)–C(8)–N(1) 119.83(13).

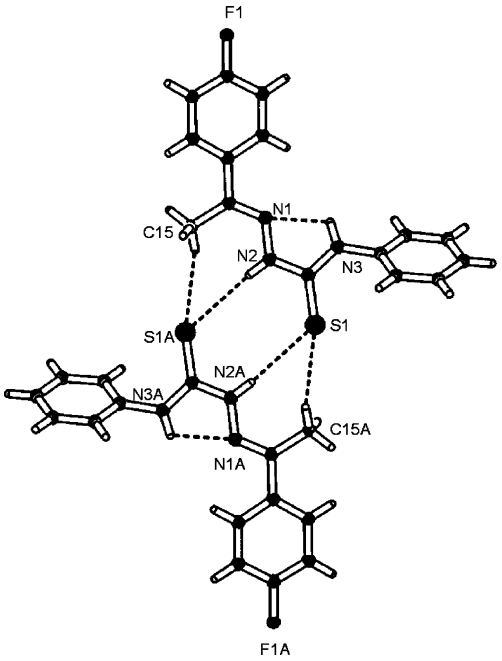


Fig. 3. A view of the hydrogen bond interactions in ligand **b**.

metallated units, in compound **4a** they are fixed in a nearly co-planar parallel mode (angle between planes 3.17(0.03)°), and at 4.57(0.03)° and 4.12(0.03)° with the P–C–C–C–P plane, so that the entire molecule may envisaged as planar with the phosphine phenyl rings jutting out from the molecular plane (see Fig. 8), whereas in compound **4c** the two metallated moieties are at an angle of 69.10°.

3. Experimental

3.1. General procedures

Solvents were purified by standard methods [44]. Chemicals were reagent grade. Lithium tetrachloropalladate was prepared in situ by treatment of palladium(II) chloride with lithium chloride in methanol. Palladium(II) acetate, palladium(II) chloride and potassium tetrachloropalladate(II) were purchased from Alfa Products. The phosphines $Ph_2P(CH_2)_2PPh_2$ (dppe), *trans*-$Ph_2P(CH{=}CH)PPh_2$(t-dpe), $Ph_2P(CH_2)_3PPh_2$ (dppp) and $Ph_2P(CH_2)_4PPh_2$- (dppb) were purchased from Aldrich-Chemie. Microanalyses were carried out at the Servicio de Análisis Elemental at the

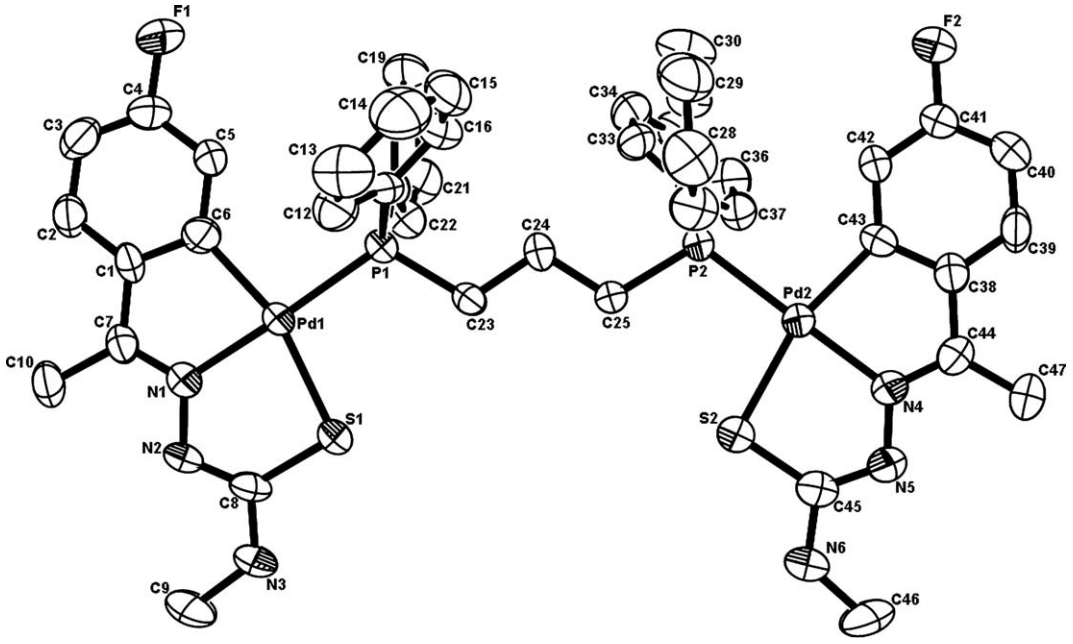


Fig. 4. An ORTEP drawing of the molecular structure for **4a** with labeling scheme (50% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths and angles (at the metal): Pd(1)–N(1) 2.039(6); Pd(1)–C(6) 2.044(8); Pd(1)–P(1) 2.261(2); Pd(1)–S(1) 2.337(2); S(1)–C(8) 1.769(8); N(2)–C(8) 1.303(10); N(3)–C(8) 1.330(10); N(1)–N(2) 1.372(8); N(1)–C(7) 1.286(9); C(1)–C(7) 1.465(11); P(1)–C(23) 1.827(7); P(1)–C(11) 1.821(8); P(1)–C(17) 1.822(8); N(1)–Pd(1)–C(6) 80.6(3); C(6)–Pd(1)–P(1) 97.5(2); P(1)–Pd(1)–S(1) 99.74(8); N(1)–Pd(1)–S(1) 82.22(18); N(1)–Pd(1)–P(1) 177.67(18); C(1)–Pd(1)–S(1) 162.8(8). Pd(2)–N(4) 2.032(6); Pd(2)–C(43) 2.051(7); Pd(2)–P(2) 2.251(2); Pd(2)–S(2) 2.331(2); S(2)–C(45) 1.763(9); N(5)–C(45) 1.306(10); N(6)–C(45) 1.332(10); N(4)–N(5) 1.365(8); N(4)–C(44) 1.309(9); C(38)–C(44) 1.479(11); P(2)–C(25) 1.827(7); P(2)–C(26) 1.821(8); P(2)–C(32) 1.822(8); N(4)–Pd(2)–C(43); C(43)–Pd(2)–P(2) 97.6(2); P(2)–Pd(2)–S(2) 98.62(8); N(4)–Pd(2)–S(2) 82.3(2); N(4)–Pd(2)–P(2) 178.53(19); C(43)–Pd(2)–S(2) 163.7(2).

Universidad of Santiago of Compostela using a Carlo Erba Elemental Analyzer Model EA1108. IR spectra were recorded as Nujol mulls or KBr discs with a Perkin–Elmer 1330, with an IR-FT Mattson Model Cygnus-100 and with a Bruker Model IFS-66V spectrophotometers. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H) or H_3PO_4 (^{31}P–$\{^1H\}$) and were recorded with Bruker AMX-300, AMX-500 and WM-250 spectrometers. All chemical shifts are reported downfield from standards. The FAB mass spectra were recorded with a Fisons Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix.

3.2. Syntheses

3.2.1. Preparation of 4-$FC_6H_4C(Me)$=NN(H)C(=S)NHMe (*a*)

4′-Fluoroacetophenone (131 mg, 9.51 mmol) and hydrochloric acid (35%, 0.65 cm^3) were added to a suspension of 4-methyl-3-thiosemicarbazide (100 mg, 9.51 mmol) in water (25 cm^3) to give a clear solution, which was stirred at room temperature for 4 h. The white solid that precipitated was filtered off, washed with cold water, and dried in air. Yield: 204 mg, 95%. Anal. Found: C, 53.5; H, 5.2; N, 18.6; S, 14.0; $C_{10}H_{12}N_3FS$ (225.3 g/mol) requires C, 53.3; H, 5.4; N, 18.6; S, 14.2%. IR (cm^{-1}): *v*(N–H) 3353m, 3219m; *v*(C=N) 1619w; *v*(C=S) 836m. ^1H NMR ($CDCl_3$, δ ppm, *J* Hz): 8.64 (s, 1H, NH), 7.59 (br, 1H, N*H*Me), 7.68 (dd, 2H, H2, H6, ^3J(H2H3) = 9.1, ^4J(H2F) = 5.3), 7.08 (t, 2H, H3, H5, ^3J(H3F) = 9.1, ^3J(H5F) = 9.1), 3.27 (d, 3H, NH*Me*, ^3J(HH) = 5.0), 2.25 (s, 3H, *Me*C=N). FAB-MS: *m*/*z* 226 $[MH]^+$.

The thiosemicarbazones **b**–**d** were synthesized following a similar procedure.

3.2.2. 4-$FC_6H_4C(Me)$=NN(H)C(=S)NHPh (*b*)

Yield: 163 mg, 95%. Anal. Found: C, 62.7; H, 4.8; N, 14.7; S, 11.1; $C_{15}H_{14}N_3FS$ (287.4 g/mol) requires C, 62.7; H, 4.9; N, 14.6; S, 11.2%. IR (cm^{-1}): *v*(N–H) 3307s, 3237m; *v*(C=N) 1618w; *v*(C=S) 840s. ^1H NMR ($CDCl_3$, δ ppm, *J* Hz): 9.35 (s, 1H, NH), 8.76 (s, 1H, N*H*Ph), 7.74 (dd, 2H, H2, H6, ^3J(H2H3) = 9.1, ^4J(H2F) = 5.3), 7.68 (d, 2H, H2′, H6′, ^3J(HH) = 7.9), 7.41 (t, 2H, H3′, H5′, ^3J(HH) = 7.9), 7.25 (t, 1H, H4′, ^3J(HH) = 7.9), 7.12 (t, 2H, H3, H5, ^3J(H3F) = 9.1, ^3J(H5F) = 9.1), 2.33 (s, 3H, *Me*C=N). FAB-MS: *m*/*z* 288 $[MH]^+$.

3.2.3. 2-$ClC_6H_4C(Me)$=NN(H)C(=S)NHPh (*c*)

Yield: 177 mg, 97%. Anal. Found: C, 59.5; H, 4.8; N, 14.0; S, 10.5; $C_{15}H_{14}ClN_3S$ (303.8 g/mol) requires C, 59.3; H, 4.6; N, 13.8; S, 10.6%. IR (cm^{-1}): *v*(N–H) 3296s, 3201m; *v*(C=N) 1594m; *v*(C=S) 800w. ^1H NMR ($CDCl_3$, δ ppm, *J* Hz): 9.34 (s, 1H, NH), 8.75 (br, 1H, N*H*Ph), 7.43 (m, 4H, H3, H4, H5, H6), 2.35 (s, 3 H, *Me*C=N). FAB-MS: *m*/*z* 304 $[M]^+$.

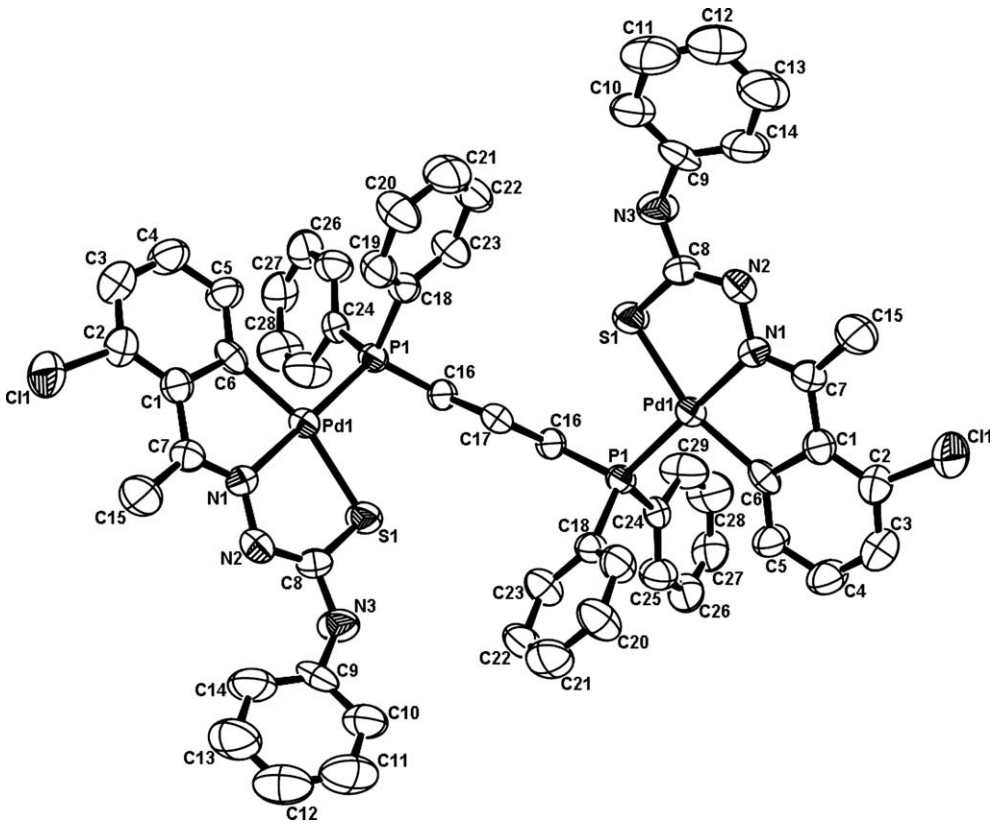


Fig. 5. An ORTEP drawing of the molecular structure for **4c** with labeling scheme (50% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths and angles (at the metal): Pd(1)–N(1) 2.020(7); Pd(1)–C(6) 2.040(10); Pd(1)–P(1) 2.274(2); Pd(1)–S(1) 2.322(3); S(1)–C(8) 1.743(10); N(2)–C(8) 1.319(11); N(3)–C(8) 1.375(11); N(1)–N(2) 1.384(10); N(1)–C(7) 1.279(11); C(1)–C(7) 1.475(12); P(1)–C(16) 1.820(9); P(1)–C(18) 1.816(9); P(1)–C(24) 1.826(9); N(1)–Pd(1)–C(6) 80.6(3); C(6)–Pd(1)–P(1) 98.6(2); P(1)–Pd(1)–S(1) 97.31(9); N(1)–Pd(1)–S(1) 83.7(2); N(1)–Pd(1)–P(1) 177.4(2); C(1)–Pd(1)–S(1) 163.7(2).

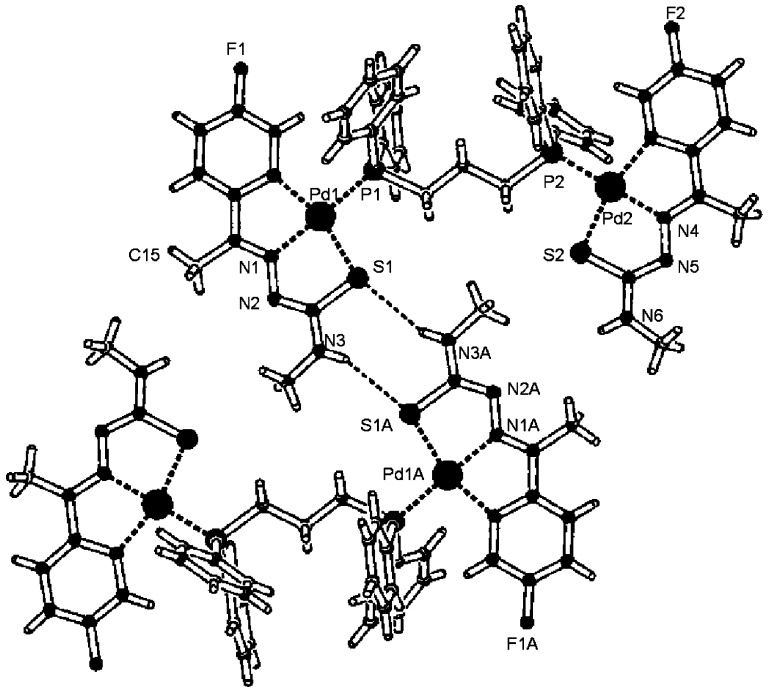


Fig. 6. Hydrogen bond interactions in compound **4a**.

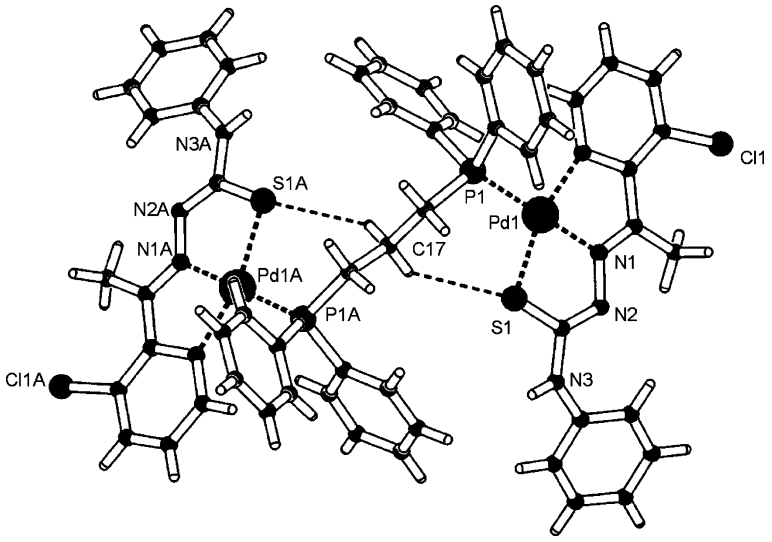


Fig. 7. Hydrogen bond interactions in compound **4c**.

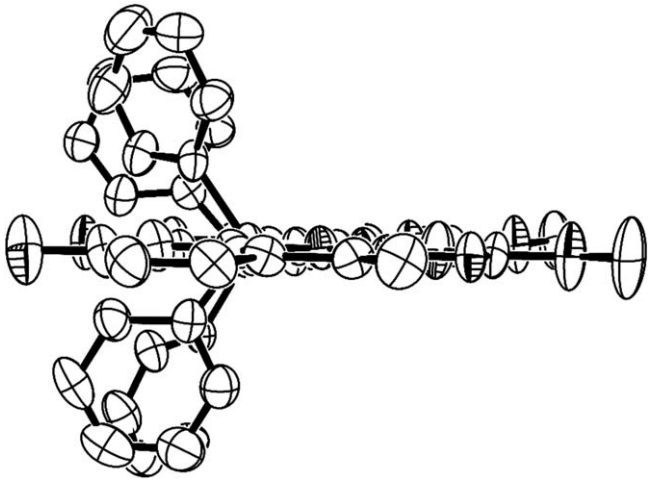


Fig. 8. An ORTEP drawing of compound **4a** showing the parallel arrangement of the cyclometallated units and the phosphine ligand, with exception of the phosphine phenyl rings.

3.2.4. Preparation of [Pd{4-$FC_6H_3C(Me)$=NN=C(S)NHMe}]$_4$ (**1a**)

Method 1. To a stirred solution of potassium tetrachloropalladate (200 mg, 0.61 mmol) in water (6 cm^3) was added ethanol (40 cm^3). The fine yellow suspension of potassium tetrachloropalladate obtained was treated with 4-FC_6H_4C(Me)=NN(H)C(=S)NHMe (**a**) (152 mg, 0.67 mmol, 10% excess). The mixture was stirred for 48 h at room temperature under nitrogen. The yellow precipitate was filtered off, washed with ethanol and dried. Yield: 192 mg, 95%. Anal. Found: C, 36.5; H, 3.1; N, 12.5; S 9.8; $C_{40}H_{40}F_4N_{12}Pd_4S_4$ (1318.8 g/mol) requires C, 36.4; H, 3.1; N, 12.7; S, 9.7%. IR (cm^{-1}): ν(N–H) 3439m; ν(C=N) 1586m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.16 (dd, 1 H, H5, ^3J(H5F) = 8.8, ^4J(H5H3) = 2.8), 6.74 (dd, 1H, H2, ^3J(H2H3) = 8.3, ^4J(H2F) = 5.5), 6.58 (td, 1H, H3, ^3J(H3F) = 8.8, ^3J(H3H2) = 8.3, ^4J(H3H5) = 2.8), 5.03 (q, 1H, N*H*Me, ^3J(NH–H) = 5.1), 3.00 (d, 3H, NH*Me*, ^3J(H–NH) = 5.1), 1.82 (s, 3H, *Me*C=N). FAB-MS: m/z 1319 $[M]^+$.

Method 2. Ligand **a** (267 mg, 1.18 mmol, 5% excess) and sodium acetate (185 mg, 2.26 mmol) were added to a stirred solution of palladium(II) chloride (200 mg, 1.13 mmol) and lithium chloride (96 mg, 2.26 mmol) in methanol (40 cm^3). The mixture was stirred for 48 h at room temperature under nitrogen. The yellow precipitate was filtered off, washed with methanol, and dried. Yield: 360 mg, 97%.

Method 3. Ligand **a** (210 mg, 0.94 mmol, 5% excess) and palladium(II) acetate (200 mg, 0.89 mmol) were added to glacial acetic acid (45 cm^3) to give a clear solution, which was heated to 60 °C under nitrogen for 24 h. After this had cooled to room temperature, the yellow precipitate was filtered off, washed with ethanol, and dried. Yield: 272 mg, 93%.

Compounds **1b** and **1c** were synthesized following a similar procedure.

3.2.5. [Pd{4-$FC_6H_3C(Me)$=NN=C(S)NHPh}]$_4$ (**1b**)

Method 1. Yield: 204 mg, 85%. Anal. Found: C, 45.9; H, 3.1; N, 10.7; S, 8.3; $C_{60}H_{48}F_4N_{12}Pd_4S_4$ (1567.0 g/mol) requires C, 46.0; H, 3.1; N, 10.7; S, 8.2%. IR (cm^{-1}): ν(N–H) 3409m, ν(C=N) 1582m. ^{1}H NMR ($CDCl_3$, d ppm, J Hz): 7.52 (d, 2H, H2′, H6′, ^3J(HH) = 7.9), 7.34 (t, 2H, H3′, H5′, ^3J(HH) = 7.9), 7.21 (dd, 1H, H5, ^3J(H5F) = 8.8, ^4J(H5H3) = 2.8), 6.90 (dd, 1H, H2, ^3J(H2H3) = 8.8, ^4J(H2F) = 5.1), 7.05 (t, 1H, H4′, ^3J(HH) = 7.9), 6.83 (s, 1H, N*H*Ph), 6.70 (td, 1H, H3, ^3J(H3F) = 8.8, ^3J(H3H2) = 8.8, ^4J(H3H5) = 2.8), 1.89 (s, 3H, *Me*C=N). FAB-MS: m/z 1568 $[M-H]^+$.

Method 2. Yield: 435 mg, 98%. *Method 3*. Yield: 295 mg, 85%.

*3.2.6. [Pd{2-ClC$_6$H$_3$C(Me)=NN=C(S)NHPh}]$_4$ (**1c**)*

Method 2. Yield: 406 mg, 92%. Anal. Found: C, 43.9; H, 2.9; N, 10.3; S, 8.0; $C_{60}H_{48}Cl_4N_{12}Pd_4S_4$ (1632.9 g/mol) requires C, 44.1; H, 3.0; N, 10.3; S, 7.9%. IR (cm^{-1}): ν(N–H) 3409m, ν(C=N) 1558s. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.49 (d, 2H, H2′, H6′, ^3J(HH) = 7.9), 7.34 (d, 2H, H3′, H5′, ^3J(HH) = 7.9), 7.30 (d, 1H, H5, ^3J(H5H4) = 7.9), 7.08 (t, 1H, H4′, ^3J(HH) = 7.9), 7.03 (d, 1H, H3, ^3J(H3H4) = 7.9), 6.93 (s, 1H, N*H*Ph), 6.66 (t, 1H, H4, ^3J(H4H3) = 7.9, ^3J(H4H5) = 7.9), 2.24 (s, 3H, *Me*C=N). FAB-MS: *m*/*z* 1634 [M–H]$^+$.

Method 3. Yield: 251 mg, 69%.

*3.2.7. Preparation of [{Pd[4-FC$_6$H$_3$C(Me)=NN=C(S)NHMe]}$_2$(μ-Ph$_2$P(CH$_2$)$_2$PPh$_2$)] (**2a**)*

The diphosphine $Ph_2P(CH_2)_2PPh_2$ (18 mg, 0.046 mmol) was added to a suspension of complex **1a** (30 mg, 0.023 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h. and the resulting yellow solid was filtered off and dried. Yield: 32.2 mg, 67%. Anal. Found: C, 52.1; H, 4.1; N, 7.7; S, 5.9; $C_{46}H_{44}F_2N_6P_2Pd_2S_2$ (1057.8 g/mol) requires C, 52.2; H, 4.2; N, 7.9; S, 6.1%. IR (cm^{-1}): ν(N–H) 3426s; ν(C=N) 1589s. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.09 (dd, 1H, H2, ^3J(H2H3) = 8.3, ^4J(H2F) = 5.5), 6.58 (td, 1H, H3, ^3J(H3F) = 8.3 Hz, ^3J(H3H2) = 8.3 Hz, ^4J(H3H5) = 2.3), 5.87 (m, 1H, H5), 2.99 (d, 3H, NH*Me*, ^3JH–NH = 4.6 Hz), 2.77 (br, 2H, P(*CH*$_2$)$_2$P), 2.51 (s, 3H, *Me*C=N). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm): 32.1s.

Compounds **2b**, **2c**, **3a**, **3c**, **4a**, **4c**, **5a** and **5c** were synthesized analogously.

*3.2.8. [{Pd{4-FC$_6$H$_3$C(Me)=NN=C(S)NHPh]}$_2$(μ-Ph$_2$P(CH$_2$)$_2$PPh$_2$)] (**2b**)*

Yield: 36.1 mg, 80%. Anal. Found: C, 56.8; H, 4.0; N, 6.9; S, 5.3; $C_{56}H_{48}F_2N_6P_2Pd_2S_2$ (1181.9 g/mol) requires C, 56.9; H, 4.1; N, 7.1; S, 5.4%. IR (cm^{-1}): ν(N–H) 3417m; ν(C=N) 1588m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.51 (d, 2H, H2′, H6′, ^3J(HH) = 7.9), 7.12 (dd, 1H, H2, ^3J(H2H3) = 8.8 Hz, ^4J(H2F) = 5.5), 6.98 (t, 1H, H4′, ^3J(HH) = 7.9), 6.71 (s, 1H, N*H*Ph), 6.57 (td, 1H, H3, ^3J(H3F) = 8.3, ^3J(H3H2) = 8.3, ^4J(H3H5) = 2.3), 6.03 (m, 1H, H5), 2.82 (br, 2H, P(*CH*$_2$)$_2$P), 2.46 (s, 3H, *Me*C=N). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm): 31.5s.

*3.2.9. [{Pd{2-ClC$_6$**H**$_3$C(Me)=NN=C(S)NHPh]}$_2$-(μ-Ph$_2$P(CH$_2$)$_2$PPh$_2$)] (**2c**)*

Yield: 31.9 mg, 71%. Anal. Found: C, 55.5; H, 4.0; N, 7.0; S, 5.2; $C_{56}H_{48}Cl_2N_6P_2Pd_2S_2$ (1214.9 g/mol) requires C, 55.4; H, 4.0; N, 6.9; S, 5.3%. IR (cm^{-1}): ν(N–H) 3400m; ν(C=N) 1557m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.50 (d, 2H, H2′, H6′, ^3J(HH) = 7.9), 7.00 (t, 1H, H4′, ^3J(HH) = 7.9), 6.87 (dd, 1H, H3, ^3J(H3H4) = 7.9, ^4J(H3H5) = 0.9), 6.68 (s, 1H, N*H*Ph), 6.40 (t, 1H, H4, ^3J(H4H3) = 7.9, ^3J(H4H5) = 7.9), 6.28 (m, 1H, H5), 2.84 (br, 5H, *Me*C=N, P(*CH*$_2$)$_2$P). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm): 31.5s.

*3.2.10. [{Pd{4-FC$_6$H$_3$C(Me)=NN=C(S)NHMe]}$_2$(μ-Ph$_2$PCH=CHPPh$_2$)] (**3a**)*

Yield: 31.3 mg, 65%. Anal. Found: C, 52.0; H, 3.9; N, 7.7; S, 5.9; $C_{46}H_{42}F_2N_6P_2Pd_2S_2$ (1055.8 g/mol) requires C, 52.3; H, 4.0; N, 8.0; S, 6.1%. IR (cm^{-1}): ν(N–H) 3421m; ν(C=N) 1585m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.10 (dd, 1H, H2, ^3J(H2H3) = 8.3, ^4J(H2F) = 5.5), 6.57 (td, 1H, H3, ^3J(H3F) = 8.3, ^3J(H3H2) = 8.3, ^4J(H3H5) = 2.3), 6.01 (m, 1H, H5), 2.96 (d, 3H, NH*Me*, ^3J(H–NH) = 4.6), 2.50 (s, 3H, *Me*C=N). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm): 31.9s.

*3.2.11. [{Pd{4-FC$_6$H$_3$C(Me)=NN=C(S)NHPh]}$_2$-(μ-Ph$_2$PCH=CHPPh$_2$)] (**3b**)*

Yield: 27.3 mg, 60%. Anal. Found: C, 56.8; H, 3.7; N, 6.9; S, 5.3; $C_{56}H_{46}F_2N_6P_2Pd_2S_2$ (1179.9 g/mol) requires C, 57.0; H, 3.9; N, 7.1; S, 5.4%. IR (cm^{-1}): ν(N–H) 3412w; ν(C=N) 1586m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.46 (d, 2H, H2′, H6′, ^3J(HH) = 7.9), 7.11 (dd, 1H, H2, ^3J(H2H3) = 8.8, ^4J(H2F) = 5.5), 6.97 (t, 1H, H4′, ^3J(HH) = 7.9), 6.65 (s, 1H, N*H*Ph), 6.54 (td, 1H, H3, ^3J(H3F) = 8.3, ^3J(H3H2) = 8.3, ^4J(H3H5) = 2.3), 6.09 (m, 1H, H5), 2.46 (s, 3H, *Me*C=N). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm): 32.5s.

*3.2.12. [{Pd{2-ClC$_6$H$_3$C(Me)=NN=C(S)NHPh]}$_2$-(μ-Ph$_2$PCH=CHPPh$_2$)] (**3c**)*

Yield: 25.0 mg, 56%. Anal. Found: C, 55.3; H, 3.8; N, 6.9; S, 5.3; $C_{56}H_{46}Cl_2N_6P_2Pd_2S_2$ (1212.8 g/mol) requires C, 55.5; H, 3.8; N, 6.9; S, 5.3%. IR (cm^{-1}): ν(N–H) 3412m; ν(C=N) 1552m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.43 (d, 2H, H2′, H6′, ^3J(HH) = 7.9), 6.98 (t, 1H, H4′, ^3J(HH) = 7.9), 6.81 (d, 1H, H3, ^3J(H3H4) = 7.9), 6.65 (s, 1H, N*H*Ph), 6.35 (m, 1H, H5), 6.26 (t, 1H, H4, ^3J(H4H3) = 7.9, ^3J(H4H5) = 7.9), 2.83 (s, 3H, *Me*C=N). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm): 32.5s.

*3.2.13. [{Pd{4-FC$_6$H$_3$C(Me)=NN=C(S)NHMe]}$_2$-(μ-Ph$_2$P(CH$_2$)$_3$PPh$_2$)] (**4a**)*

Yield: 27.1 mg, 56%. Anal. Found: C, 52.6; H, 4.3; N, 7.7; S, 5.9; $C_{47}H_{46}F_2N_6P_2Pd_2S_2$ (1071.8 g/mol) requires C, 52.7; H, 4.3; N, 7.8; S, 6.0%. IR (cm^{-1}): ν(N–H) 3427m; ν(C=N) 1583m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.01 (dd, 1H, H2, ^3J(H2H3) = 8.3, ^4J(H2F) = 5.5), 6.51 (td, 1H, H3, ^3J(H3F) = 8.3, ^3J(H3H2) = 8.3, ^4J(H3H5) = 2.8), 5.97 (ddd, 1H, H5, ^3J(H5F) = 9.2, ^4J(H5P) = 4.2, ^4J(H3H5) = 2.8), 4.78 (q, 1H, N*H*Me, ^3J(NH–H) = 5.1), 2.99 (d, 3H, NH*Me*, ^3J(H–NH) = 5.1), 2.53 (m, 2H, PC*H*$_2$CH$_2$C*H*$_2$P), 2.35 (s, 3H, *Me*C=N), 2.09 (br, 1H, PCH$_2$C*H*$_2$CH$_2$P). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm): 27.1s.

*3.2.14. [{Pd{4-FC$_6$H$_3$C(Me)=NN=C(S)NHPh]}$_2$-(μ-Ph$_2$P(CH$_2$)$_3$PPh$_2$)] (**4b**)*

Yield: 35.3 mg, 77%. Anal. Found: C, 57.0; H, 4.1; N, 6.9; S, 5.2; $C_{57}H_{50}F_2N_6P_2Pd_2S_2$ (1196.0 g/mol) requires C, 57.2; H, 4.2; N, 7.0; S, 5.4%. IR (cm^{-1}): ν(N–H)

3419m; ν(C=N) 1587m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.52 (d, 2H, H2′, H6′, ^3J(HH) = 7.9 Hz), 7.08 (dd, 1H, H2, ^3J(H2H3) = 8.3, ^4J(H2F) = 5.5), 6.99 (t, 1H, H4′, ^3J(HH) = 7.9), 6.72 (s, 1H, N*H*Ph), 6.54 (td, 1H, H3, ^3J(H3F) = 8.3, ^3J(H3H2) = 8.3, ^4J(H3H5) = 2.8), 6.02 (ddd, 1H, H5, ^3J(H5F) = 9.2, ^4J(H5P) = 4.2, ^4J(H3H5) = 2.8), 2.59 (m, 2H, P*CH*$_2$CH$_2$*CH*$_2$P), 2.43 (s, 3H, *Me*C=N), 2.21 (br, 1H, PCH$_2$*CH*$_2$CH$_2$P). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm): 26.8s.

3.2.15. [{Pd{2-ClC$_6$H$_3$C(Me)=NN=C(S)NHPh]}$_2$-(μ-Ph$_2$P(CH$_2$)$_3$PPh$_2$)] (**4c**)

Yield: 18.5 mg, 41%. Anal. Found: C, 55.9; H, 4.2; N, 6.9; S, 5.1; $C_{57}H_{50}Cl_2N_6P_2Pd_2S_2$ (1228.9 g/mol) requires C, 55.7; H, 4.1; N, 6.8; S, 5.2%. IR (cm^{-1}): ν(N–H) 3392m; ν(C=N) 1556m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.50 (d, 2H, H2′, H6′, ^3J(HH) = 7.9), 7.00 (t, 1H, H4′, ^3J(HH) = 7.9), 6.85 (dd, 1H, H3, ^3J(H3H4) = 7.9, ^4J(H3H5) = 0.9), 6.73 (s, 1H, N*H*Ph), 6.45 (t, 1H, H4, ^3J(H4H3) = 7.9, ^3J(H4H5) = 7.9), 6.32 (ddd, 1H, H5, ^3J(H5H4) = 7.9, ^4J(H5P) = 4.6, ^4J(H5H3) = 0.9), 2.81 (s, 3H, *Me*C=N), 2.57 (m, 2H, P*CH*$_2$CH$_2$*CH*$_2$P), 2.24 (br, 1H, PCH$_2$*CH*$_2$CH$_2$P). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm): 26.8s.

3.2.16. [{Pd{4-FC$_6$H$_3$C(Me)=NN=C(S)NHMe]}$_2$-(μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$)] (**5a**)

Yield: 11.3 mg, 43%. Anal. Found: C, 53.2; H, 4.6; N, 7.5; S, 5.8; $C_{48}H_{48}F_2N_6P_2Pd_2S_2$ (1085.9 g/mol) requires C, 53.1; H, 4.5; N, 7.7; S, 5.9%. IR (cm^{-1}): ν(N–H) 3428s; ν(C=N) 1584m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.02 (dd, 1H, H2, ^3J(H2H3) = 8.3, ^4J(H2F) = 5.5), 6.51 (td, 1H, H3, ^3J(H3F) = 8.3, ^3J(H3H2) = 8.3, ^4J(H3H5) = 2.8), 6.01 (ddd, 1H, H5, ^3J(H5F) = 9.2, ^4J(H5P) = 4.2, ^4J(H3H5) = 2.8), 4.76 (br, 1H, N*H*Me), 2.97 (d, 3H, NH*Me*, ^3J(H–NH) = 4.6), 2.35 (s, 3H, *Me*C=N), 2.28 (br, 2H, P*CH*$_2$CH$_2$CH$_2$*CH*$_2$P), 1.74 (br, 2 H, PCH$_2$*CH*$_2$*CH*$_2$CH$_2$P). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm): 28.7s.

3.2.17. [{Pd{4-FC$_6$H$_3$C(Me)=NN=C(S)NHPh]}$_2$-(μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$)] (**5b**)

Yield: 29.4 mg, 64%. Anal. Found: C, 57.7; H, 4.4; N, 6.8; S, 5.2; $C_{58}H_{52}F_2N_6P_2Pd_2S_2$ (1210.0 g/mol) requires C, 57.6; H, 4.3; N, 6.9; S, 5.3%. IR (cm^{-1}): ν(N–H) 3421m; ν(C=N) 1587m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.49 (d, 2H, H2′, H6′, ^3J(HH) = 7.9), 7.09 (dd, 1H, H2, ^3J(H2H3) = 8.3, ^4J(H2F) = 5.5), 6.96 (t, 1H, H4′, ^3J(HH) = 7.9), 6.75 (s, 1H, N*H*Ph), 6.54 (td, 1H, H3, ^3J(H3F) = 8.3, ^3J(H3H2) = 8.3, ^4J(H3H5) = 2.3), 6.06 (m, 1H, H5), 2.44 (s, 3H, *Me*C=N), 2.35 (br, 2H, P*CH*$_2$CH$_2$CH$_2$*CH*$_2$P), 1.81 (br, 2H, PCH$_2$*CH*$_2$*CH*$_2$CH$_2$P). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm): 28.7s.

3.2.18. [{Pd{2-ClC$_6$H$_3$C(Me)=NN=C(S)NHPh]}$_2$-(μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$)] (**5c**)

Yield: 22.3 mg, 49%. Anal. Found: C, 55.8; H, 4.1; N, 6.9; S, 5.3; $C_{58}H_{52}Cl_2N_6P_2Pd_2S_2$ (1242.9 g/mol) requires C, 56.0; H, 4.2; N, 6.8; S, 5.2%. IR (cm^{-1}): ν(N–H) 3406m; ν(C=N) 1557m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.47 (d, 2H, H2′, H6′, ^3J(HH) = 7.9), 6.98 (t, 1H, H4′, ^3J(HH) = 7.9), 6.84 (dd, 1H, H3, ^3J(H3H4) = 7.9, ^4J(H3H5) = 0.9), 6.75 (s, 1H, N*H*Ph), 6.44 (t, 1H, H4, ^3J(H4H3) = 7.9, ^3J(H4H5) = 7.9), 6.35 (ddd, 1H, H5, ^3J(H5H4) = 7.9, ^4J(H5P) = 4.6, ^4J(H5H3) = 0.9), 2.82 (s, 3H, *Me*C=N), 2.34 (m, H, P*CH*$_2$CH$_2$CH$_2$*CH*$_2$P), 1.81 (br, 2H, PCH$_2$*CH*$_2$*CH*$_2$CH$_2$P). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm): 28.7s.

3.3. Crystal structures

Crystals of ligand **b** and of complexes **4a** · 3$CHCl_3$ and **4c** · $CHCl_3$ were mounted on a glass fiber and transferred to the diffractometer. For **b** room temperature X-ray data was collected on a CAD4 Enraf Nonius diffractometer using graphite monochromated Cu Kα radiation by the omega/2-theta method. Three dimensional, room temperature X-ray data, **4a** and **4d**, were collected with Bruker SMART CCD diffractometer by the omega scan method, using monochromated Mo Kα radiation. All the measured reflections were corrected for Lorentz and polarization effects and for absorption by semiempirical methods based on symmetry-equivalent and repeated reflections [T_{max}/T_{min} = 0.8539/0.3554 (**b**), 0.9214/0.7798 (**4a**) and 0.8795/0.7785 (**4c**)]. 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_1 = 0.0407 (**b**), 0.0658 (**4a**) and 0.0676 (**4c**) (observed data, F), and wR_2 = 0.1271 (**b**), 0.1983 (**4a**) and 0.2127 (**4c**) (all unique data, F^2), with allowance for thermal anisotropy of all non-hidrogen atoms. Minimum and maximum final electron densities: −0.228 and 0.234 (**b**), −1.337 and 1.496 (**4a**), −1.596 and 0.913 e Å^{-3} (**4c**). The structure solutions and refinements were carried out with the SHELX-97 [45] program package.

4. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. 291906 (**b**), 291907 (**4a**), 291908 (**4c**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgements

We thank the DGESIC (Ministerio de Ciencia y Tecnología) Proyecto BQU2002-04533-C02-01 and the Xunta de Galicia, incentive PGIDIT03PXIC20912PN, for financial support. J. Martínez acknowledges a fellowship from the Ministerio de Ciencia y Tecnología (Grant No. PB98-0638-C02-01/02).

References

[1] M.I. Bruce, Angew. Chem. Int. Ed. Engl. 16 (1977) 73.
[2] (a) I. Omae, Chem. Rev. 79 (1979) 287;
(b) I. Omae, Coord. Chem. Rev. 83 (1988) 137.
[3] I. Omae, Organometallic Intramolecular-coordination Compounds, Elsevier, Amsterdam, 1986.
[4] V.V. Dunina, O.A. Zalevskaya, V.M. Potapov, Russ. Chem. Rev. 57 (1988) 250–269.
[5] G.R. Newkome, W.E. Puckett, W.K. Gupta, G.E. Kiefer, Chem. Rev. 86 (1986) 451.
[6] J. Dupont, M. Pfeffer, J. Spencer, Eur. J. Inorg. Chem. (2001) 1917.
[7] J. Tsuji, Palladium Reagents and Catalysts, Wiley, Chichester, 1996.
[8] M. Pfeffer, Recl. Trav. Chim. Pays Bas 109 (1990) 567.
[9] J. Spencer, M. Pfeffer, Avd. Organomet. Chem. 3 (1994) 1.
[10] I. Omae, Applications of Organometallic Compounds, Wiley, Chichester, 1998.
[11] C.R.. Sinha, D. Bandyopadhyay, A. Chakravorty, J. Chem. Soc., Chem. Commun. (1988) 468.
[12] A.D. Ryabov, R. Van Eldik, G. Le Borgne, M. Pfeffer, Organometallics 12 (1993) 1386.
[13] M. Pfeffer, J.P. Sutter, M.A. Rottevel, A. De Cian, J. Fisher, Tetrahedron 48 (1992) 2440.
[14] A. Bose, C.H. Saha, J. Mol. Catal. 49 (1989) 271.
[15] J. Albert, A. González, J. Granell, R. Moragas, C. Puerta, P. Valegra, Organometallics 16 (1997) 3775.
[16] A.D. Ryabov, Chem. Rev. 90 (1990) 403.
[17] D.J. Cárdenas, A.M. Echavarren, M.C.R. de Arellano, Organometallics 18 (1999) 3337.
[18] J. Albert, A. González, J. Granell, R. Moragas, C. Puerta, P. Valegra, Organometallics 16 (1997) 3775.
[19] G. García-Herbosa, A. Muñoz, D. Miguel, S. García-Granda, Organometallics 13 (1994) 1775.
[20] T.C. Cheung, K.K. Cheung, S.M. Peng, C.H. Che, J. Chem. Soc., Dalton Trans. (1996) 1645.
[21] C. Cativiela, L.R. Falvello, J.C. Ginés, R. Navarro, E.P. Urriolabeitia, New J. Chem. 25 (2001) xxxx.
[22] A. Fernández, D. Vázquez-García, J.J. Fernández, M. López-Torres, A. Suárez, S. Castro-Juiz, J.M. Vila, New J. Chem. 26 (2002) 398.
[23] A. Amoedo, M. Graña, J. Martinez, T. Pereira, M. Lopez-Torres, A. Fernandez, J.J. Fernandez, J.M. Vila, Eur. J. Inorg. Chem. (2002) 613.
[24] J.M. Vila, T. Pereira, J.M. Ortigueira, M. Graña, D. Lata, A. Suarez, J.J. Fernández, A. Fernández, M. Lápez-Torres, H. Adams, J. Chem. Soc., Dalton Trans. (1999) 4193.
[25] J.M. Vila, T. Pereira, J.M. Ortigueira, M. Lopez-Torres, A. Castiñeiras, D. Lata, J.J. Fernandez, A. Fernandez, J. Organomet. Chem. 556 (1998) 21.
[26] S. Tollari, G. Palmisano, G. Dematrin, M. Grassi, S. Magnaghi, S. Cenini, J. Organomet. Chem. 488 (1995) 79.
[27] A. Bacchi, M. Carcelli, M. Costa, P. Pelagatti, C. Pelizzi, G. Pelizzi, J. Chem. Soc., Dalton Trans. (1996) 4239.
[28] (a) J.M. Vila, M.T. Pereira, J.M. Ortigueira, D. Lata, M. Lápez-Torres, J.J. Fernández, A. Fernández, H. Adams, J. Organomet. Chem. 566 (1998) 93;
(b) J.M. Vila, T. Pereira, J.M. Ortigueira, A. Amoedo, M. Graña, G. Alberdi, M. Lopez-Torres, A. Fernandez, J. Organomet. Chem. 663 (2002) 239.
[29] J. Martinez, M.T. Pereira, I. Buceta, G. Alberdi, A. Amoedo, J.J. Fernandez, M. Lopez-Torres, J.M. Vila, Organometallics 22 (2003) 5581.
[30] L. Adrio, A. Amoedo, J.M. Antelo, J.J. Fernández, J. Martínez, J.M. Ortigueira, M. Pereira, J.M. Vila, Z. anorg. allg. Chem. 631 (2005) 2204.
[31] T.S. Lobana, A. Sánchez, J.S. Casas, A. Castiñeiras, J. Sordo, M.S. García-Tasende, E.M. Vázquez-López, J. Chem. Soc., Dalton Trans. (1997) 4289.
[32] D.X. West, D.X.J.S. Ives, G.A. Bain, A.E. Liberta, J. Valdés-Martínez, K.H. Ebert, S. Hernández-Oertega, Polyhedron 16 (1997) 1995.
[33] H. Onoue, I. Moritani, J. Organomet. Chem. 43 (1972) 431.
[34] H. Onoue, K. Minami, K. Nakawaga, Bull. Chem. Soc. Jpn. 43 (1970) 3480.
[35] D. Kovala-Demertzi, A. Domopoulou, M.A. Demertzis, C.P. Raptopoulou, A. Terzis, Polyhedron 13 (1994) 1917.
[36] D. Kovala-Demertzi, A. Domopoulou, M.A. Demertzis, J. Valdés-Martínez, S. Hernández-Ortega, G. Espinosa-Pérez, D.X. West, M.M. Salberg, G.A. Bain, P.D. Bloom, Polyhedron 15 (1996) 665.
[37] J. Vicente, J.A. Abad, A.D. Frankland, M.C. Ramirez de Arellano, Chem. Eur. J. 5 (1999) 3067.
[38] P.S. Pregosin, R.W. Kuntz, in: P. Diehl, E. Fluck, R. Kosfeld (Eds.), ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes, Springer, Berlin, 1979.
[39] J. Albert, M. Gómez, J. Granell, J. Sales, Organometallics 9 (1990) 1405.
[40] J. Albert, J. Granell, J. Sales, M. Font-Bardía, X. Solans, Organometallics 14 (1995) 1393.
[41] L. Pauling, The Nature of Chemical Bond, third ed., Cornell University Press, New York, 1960.
[42] J. Selbin, K. Abboud, S.F. Watkins, M.A. Gutirérrez, F.R. Fronczek, J. Organomet. Chem. 241 (1983) 259.
[43] C. Navarro-Ranninger, I. López-Solera, A. Alvarez-Valdés, J.H. Rodríguez-Ramos, J.R. Masaguer, J.L. García-Ruano, Organometallics 12 (1993) 4104.
[44] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, fourth ed., Butterworth-Heinemann, London, 1996.
[45] G.M. Sheldrick, SHELX-97, An Integrated System for Solving and Refining Crystal Structures from Diffraction Data, University of Göttingen, Germany, 1997.