Available online at www.sciencedirect.com
ScienceDirect
Polyhedron 26 (2007) 4567–4572
POLYHEDRON
www.elsevier.com/locate/poly

Reactivity of tetranuclear complexes of Pd(II) with potentially homo- and heterobidentate ligands

Jesús J. Fernández [a,*], Alberto Fernández [a], Digna Vázquez-García [a], Margarita López-Torres [a], Antonio Suárez [a], José M. Vila [b,*]

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

Received 30 April 2007; accepted 9 June 2007
Available online 27 June 2007

Abstract

Reaction of the cyclometallated compounds $[Pd\{2,3,4\text{-}(MeO)_3C_6HC(H)=N[2\text{-}(O)\text{-}5\text{-}RC_6H_3]\}]_4$ (**1a**: R = H, **1b**: R = ^{t}Bu) with the phosphine $PPh_2[2\text{-}(COH)C_6H_4]$, in a complex/phosphine 1:4 molar ratio gave the mononuclear cyclometallated complexes $[\{Pd\{2,3,4\text{-}(MeO)_3C_6HC(H)=N[2\text{-}(O)\text{-}5\text{-}RC_6H_3\}\}\{PPh_2[2\text{-}(HOC)C_6H_4]\}]$ (**2a**: R = H; **2b**: R = ^{t}Bu), upon cleavage of the tetranuclear structure. Treatment of complex **1a** with the diarsine $AsPh_2(CH_2)_2Ph_2As$ (dppae) in a 1:2 or 1:4 molar ratio only yielded the dinuclear compound $[\{Pd\{2,3,4\text{-}(MeO)_3C_6HC(H)=N[2\text{-}(O)C_6H_4]\}\}_2\{\mu\text{-}AsPh_2(CH_2)_2Ph_2As\}]$ (**3a**), regardless the molar ratio used. Reaction of the cyclometallated tetramers with $Ph_2P(CH_2)_2Ph_2As$ (arphos) in a 1:4 molar ratio gave the mononuclear cyclometallated complexes $[Pd\{2,3,4\text{-}(MeO)_3C_6HC(H)=N[2\text{-}(O)C_6H_4]\}\{PPh_2(CH_2)_2Ph_2As\text{-}P\}]$ (**4a**) and $[Pd\{2,3,4\text{-}(MeO)_3C_6HC(H)=N[2\text{-}(O)\text{-}5\text{-}^tBuC_6H_3]\}\{PPh_2(CH_2)_2Ph_2As\text{-}P\}]$ (**4b**), with the P, As ligand coordinated through the phosphorus atom, as air-stable solids. Treatment of **1a** with arphos in a 1:2 molar ratio gave the dinuclear complex $[\{Pd\{2,3,4\text{-}(MeO)_3C_6HC(H)=N[2\text{-}(O)C_6H_4]\}\}_2\{\mu\text{-}PPh_2(CH_2)_2Ph_2As\}]$ (**5a**). Reaction of **1b** with the diphosphine $Ph_2P(C_6H_4)O(C_6H_4)PPh_2$ gave the dinuclear compound $[\{Pd\{2,3,4\text{-}(MeO)_3C_6HC(H)=N[2\text{-}(O)\text{-}^tBuC_6H_3]\}\}_2\{\mu\text{-}PPh_2(C_6H_4)O(C_6H_4)Ph_2P\}]$ (**6b**) for all the complex **1b**/phosphine molar ratios tested. Reaction of the cyclometallated tetramer **1a** with $PPh_2[4\text{-}(NMe_2)C_6H_4]$ (in 1:2 or 1:4 molar ratio) produced the mononuclear cyclometallated complex $[Pd\{2,3,4\text{-}(MeO)_3C_6HC(H)=N[2\text{-}(O)C_6H_4]\}\{PPh_2[4\text{-}(NMe_2)C_6H_4]\}]$ (**7a**) as an air-stable solid.

Keywords: Palladium; Metallation; Phosphines; As ligand; [P, As] ligand; [P, N] ligand

1. Introduction

Cyclometallation and phosphines constitute relevant topics in organometallic chemistry and several reviews covering the former have appeared [1–8]. Tertiary mono- and polydentate phosphine ligands stabilize a great variety of metal complexes in different oxidation states and phosphine containing complexes are good catalysts [9,10], e.g., in the hydrogenation of aldehydes [11] and aromatic ketones [12] or the carbonylation of metal–methyl bonds [13]; they are also useful as therapeutic agents in anticancer drugs [14] or as structural fragments on polystyrene-immobilized catalysts [15]. Numerous reactions of cyclometallated compounds with tertiary phosphines have been reported by us and others [16].

In the past, we have been interested in palladium(II) and platinum(II) cyclometallated complexes derived from [C, N, X] (X = O, S) terdentate ligands. Those derived from [C, N, S] thiosemicarbazones **I** (Fig. 1) [17–20] or from Schiff bases with phenolate oxygen atoms **II** (Fig. 1) [21,22] show tetranuclear structures, with eight-membered Pd_4X_4 cores (X = O, S), bearing two different types of P–X bonds: $P\text{–}X_{chelating}$ and $P\text{–}X_{bridging}$, which bind the ligand tightly to the metal centre. The reaction of these compounds with mono and bidentate tertiary phosphines

* Corresponding authors. Tel.: +34 9 8152800; fax: +34 981 595012 (J.M. Vila), +34 981 167065 (J.J. Fernández).
E-mail addresses: qiluaafl@udc.es (J.J. Fernández), qideport@usc.es (J.M. Vila).

0277-5387/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2007.06.012

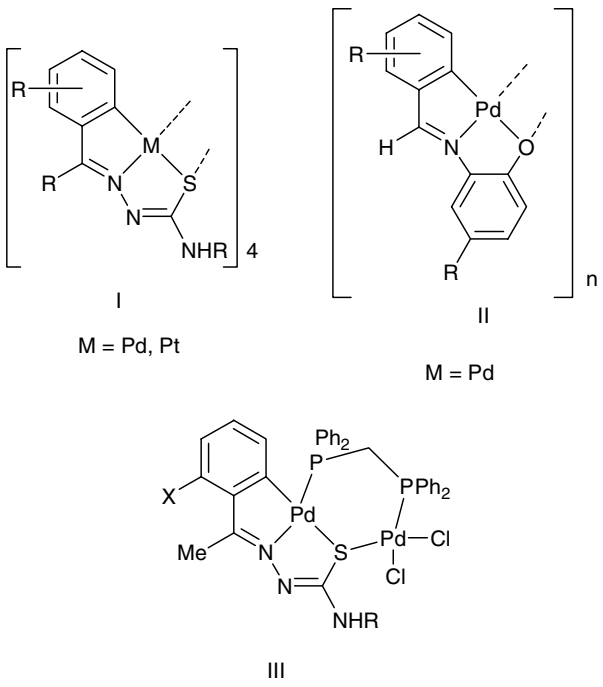


Fig. 1. Cyclometallated complexes with [C, N, X] (X = O, S) ligands.

brings about opening of the tetranuclear structure due to the P–$X_{bridging}$ bond cleavage, whereas the P–$X_{chelating}$ bond persists, even when large excess of the phosphine was used, putting forward its unusual strength. More recently, we have shown that reaction of the tetranuclear tetramers derived from thiosemicarbazones (X = S) with bis(diphenylphosphino)methane caused cleavage of the tetranuclear structure to give new mononuclear complexes, in which the phosphine is monodentate, where one phosphorus atom is uncoordinated. These complexes represent a new class of bidentate [P, S] chelating metalloligands capable of coordinating a second metal centre and, therefore, may be used as building blocks in the construction of polynuclear structures **III** (Fig. 1) [23].

We reasoned that the similar behavior of terdentate [C, N, O] Schiff base species towards nucleophiles, in terms of a strong P–$O_{chelating}$ bond, could be used to explore a new range of compounds upon reaction of the former with phosphines, arsines, and mixed phosphorus/arsenic ligands. Therefore, herein, we report the reactivity of complexes $[Pd\{2,3,4\text{-}(MeO)_3C_6HC(H)=N[2\text{-}(O)\text{-}5\text{-}RC_6H_3]\}]_4$ (**1a**: R = H, **1b**: R = ^{t}Bu) with bidentate [P, O], [P, As], [P, P], [As, As] and [P, N] ligands.

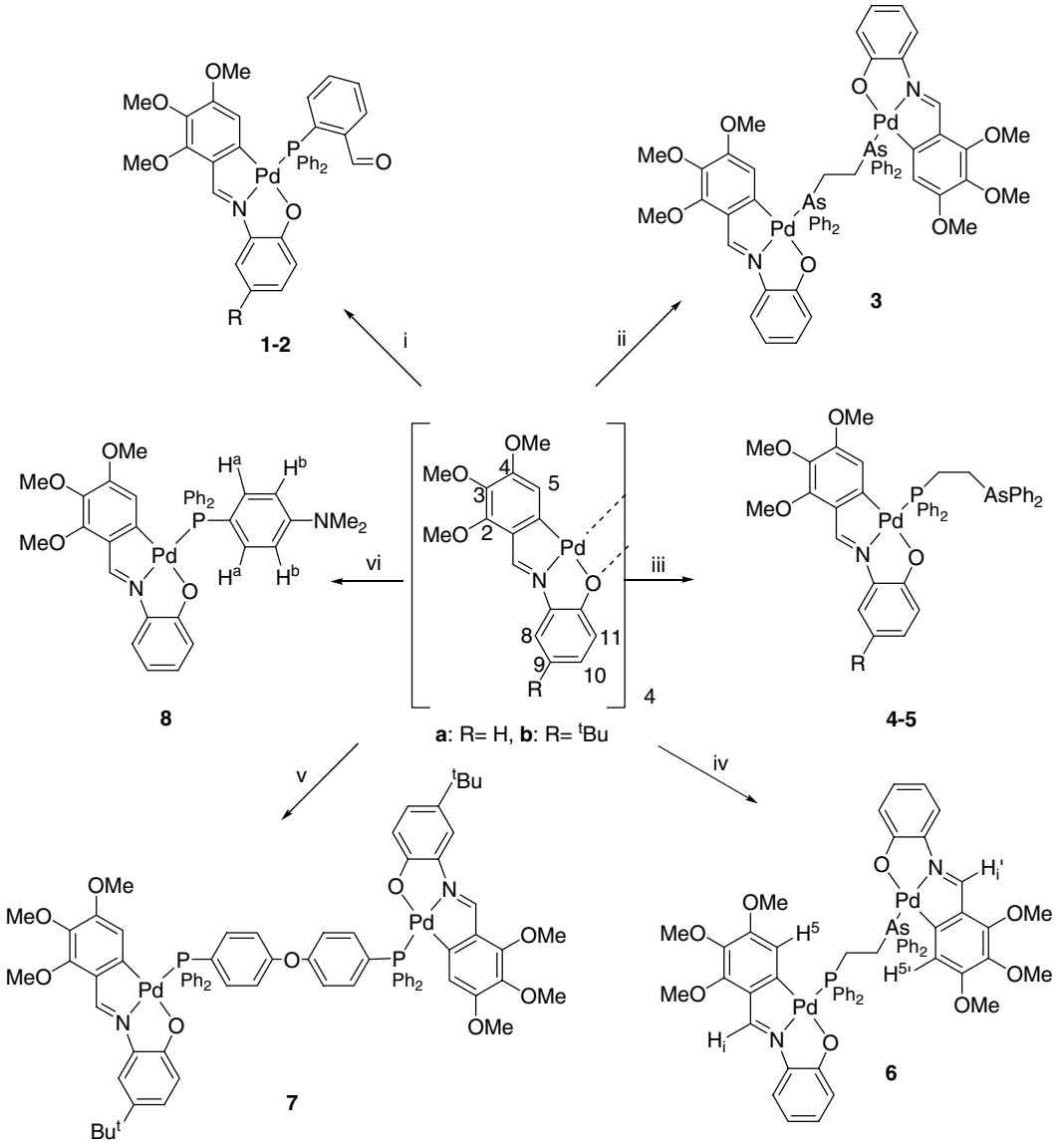
2. Results and discussion

The compounds and reactions are shown in Scheme 1. The compounds were characterised by IR and by ^{1}H, ^{31}P–{^{1}H} spectroscopy and, in part, FAB mass spectrometry; the elemental analysis (C, H, N) supports the expected elemental composition (data in Section 4).

Treatment of **1a** and **1b** with $PPh_2[2\text{-}(COH)C_6H_4]$ in 1:4 molar ratio or with $Ph_2P[4\text{-}(NMe_2)C_6H_4]$ in 1:2 or 1:4 molar ratios, afforded the mononuclear complexes $[Pd\{2,3,4\text{-}(MeO)_3C_6HC(H)=N[2\text{-}(O)C_6H_4\}\{PPh_2[2\text{-}HOC)C_6H_4]\}]$ (**2a**) $[Pd\{2,3,4\text{-}(MeO)_3C_6HC(H)=N[2\text{-}(O)\text{-}5\text{-}^tBuC_6H_3\}\{PPh_2[2\text{-}(HOC)C_6H_4]\}]$ (**2b**) and $[Pd\{2,3,4\text{-}(MeO)_3C_6HC(H)=N[2\text{-}(O)C_6H_4]\}\{PPh_2[4\text{-}(NMe_2)C_6H_4]\}]$ (**7a**), respectively, as air stable solids, in which the tetrameric structure was cleaved after P–$O_{bridging}$ bond cleavage. Coordination of the palladium atom to the C=N moiety was confirmed by the shift to lower wavenumbers of the ν(C=N) band, as compared to the free ligand [21,24,25]. Absence of the ν(OH) band was in agreement with the presence of a phenolate oxygen bonded to the palladium atom [21,22]. These findings were observed for the remaining compounds and shall not be discussed further (see Section 4). The proton resonances were unequivocally assigned (see Section 4); those ascribed to *H*5 and *H*C=N appeared as doublets due to coupling with the ^{31}P nucleus with *J* values of *ca.* 4 and 10 Hz, respectively. In the ^{31}P–{^{1}H} spectra the phosphorus resonance signal appeared as a singlet *ca.* δ 33.0 ppm; these findings were in agreement with a phosphorus *trans* to nitrogen arrangement [21,26–30]. The signals assigned to the *H*5 and 4-O*Me* protons were shifted to lower frequency, as compared to the cyclometallated complexes **1a** and **1b**, due to shielding of phosphine phenyl rings. We have previously observed similar shifts in related complexes, confirming the relative *trans* disposition of the nitrogen atom and the phosphine ligand [17,31]. The FAB mass spectra showed the cluster of peaks characteristic of the $[M]^+$ fragment at 680, **2a**, 738, **2b**, and 697, **7a** uma.

Reaction of **1a** with $AsPh_2(CH_2)_2Ph_2As$ (dppae) in a 1:2 ratio in acetone, gave the dinuclear cyclometallated complex $[\{Pd\{2,3,4\text{-}(MeO)_3C_6HC(H)=N[2\text{-}(O)C_6H_4]\}\}_2\{\mu\text{-}AsPh_2(CH_2)_2Ph_2As\}]$ (**3a**) as an air stable solid. In the ^{1}H NMR spectrum the *H*C=N and H^5 proton resonances appeared as singlets at δ 7.57 and 5.51 ppm, respectively. The H5 and 4-O*Me* resonances were shifted towards lower frequency by *ca.* 0.2 and 1.2 ppm, respectively, due to the shielding effects of the diarsine phenyl rings. Only one set of signals was observed for the proton resonances, indicative of the symmetrical nature of the compounds. The FAB mass spectrum showed two clusters of peaks centred at 1271 and 878 uma, assigned to the molecular ion and to loss of one cyclometallated unit, respectively. Compound **3a** was also isolated when excess dppa was used, establishing the strength of the Pd–$O_{chelating}$ bond, which was not cleaved even under these reaction conditions.

Treatment of **1a** or **1b** with $Ph_2P(CH_2)_2Ph_2As$ (arphos) in the appropriate molar ratio afforded compounds $[Pd\{2,3,4\text{-}(MeO)_3C_6HC(H)=N[2\text{-}(O)C_6H_4]\}\{PPh_2(CH_2)_2Ph_2As\text{-}P\}]$ (**4a**), $[Pd\{2,3,4\text{-}(MeO)_3C_6HC(H)=N[2\text{-}(O)\text{-}5\text{-}^tBuC_6H_3]\}\{PPh_2(CH_2)_2Ph_2As\text{-}P\}]$ (**4b**), and $[\{Pd\{2,3,4\text{-}(MeO)_3C_6HC(H)=N[2\text{-}(O)C_6H_4]\}\}_2\{\mu\text{-}PPh_2(CH_2)_2Ph_2As\}]$ (**5a**). Coordination of the ligand through the phosphorus atom was confirmed by: (a) the multiplicity of the *H*5 and *H*C=N



Scheme 1. (i) Phosphine (acetone, 1:4 molar ratio), (ii) dppae (acetone, 1:2 or 1:4 molar ratio), (iii) arphos (acetone, 1:4 molar ratio), (iv) arphos (acetone, 1:2 molar ratio), (v) diphosphine (acetone, 1:2 or 1:4 molar ratio), (vi) phosphine (dichloromethane, 1:2 or 1:4 molar ratio).

resonances, which were observed as doublets by coupling to the ^{31}P nucleus; (b) the chemical shift of the phosphorus resonance signal at δ 32.5 (**4a**), δ 33.4 (**4b**) and δ 34.0 (**5a**), downfield shifted from its position in the spectrum of the free phosphine, and also in agreement with a phosphorus *trans* to nitrogen coordination to the metal center [21,26–30]. The asymmetric nature of compound **5a** was evidenced by the two distinct sets of proton signals observed for both cyclometallated moieties. Accordingly, two doublet resonances at δ 8.14 and δ 5.42, were assigned to the *H*5 and *HC*=N protons, respectively, coupled to the ^{31}P nucleus with [$^4J(H_iP) = 10.5$ Hz, $^4J(H^5P) = 3.9$ Hz], and two singlets were ascribed to the *H*5′ and *H*′C=N protons at δ 7.58 and δ 5.56, respectively.

In the FAB mass spectra the set of peaks at 834 and 890 uma, for **4a** and **4b**, respectively, were assigned to the $[MH]^+$ ions; their isotopic pattern confirmed the mononuclear formula of the complexes. For compound **5a** a cluster of peaks at 1226 uma was consistent with a dinuclear formula.

Treatment of **2b** with $Ph_2P(C_6H_4)O(C_6H_4)Ph_2P$ in a 1:2 or 1:4 molar ratio at room temperature in acetone gave the dinuclear compound [{Pd{2,3,4-$(MeO)_3C_6HC(H)$=N[2-(O)-^{t}BuC_6H_3]}}$_2${μ-$PPh_2(C_6H_4)O(C_6H_4)Ph_2P$}] (**6b**) (the use of excess phosphine only gave **6b** and unreacted **2b**), after column chromatography (see Section 4). Therefore, the diphosphine could not behave as monodentate through only one phosphorus atom. Thus, both sets of *HC*=N and H5 resonances showed coupling to the phosphorus nuclei [$^4J(HP) = 10.7$ and $^4J(HP) = 3.7$ Hz], and the ^{31}P–{^1H} NMR spectrum revealed a singlet at δ 28.2, in agreement with equivalent phosphorus nuclei.

3. Conclusions

We have shown that Schiff base ligands derived from 2-aminophenols secure three metal coordination sites in cyclometallated palladium(II) compounds and leave but one bonding site for further reaction with nucleophiles, such as tertiary phosphines or arsines. Consequently, the $P–O_{chelating}$ bond remained throughout all the processes in this study, and it was not cleaved upon reaction with the nucleophiles tested. Additional coordinating atoms on the phosphine ligand, such as nitrogen or oxygen, did not show any relevant bonding properties. However, diphosphines or diarsines could bridge two cyclometallated moieties, rendering dinuclear species.

In the case of arphos, this ligand showed to be versatile in its coordination to the cyclometallated complexes **1a** and **1b**. Thus, by adjusting the relative molar ratio, mono- or dinuclear complexes could be prepared, with the ligand behaving as mono- or bidentate, respectively. Still, arphos did not act as a chelating ligand, regardless of the reaction conditions employed.

4. Experimental

4.1. General procedures

Solvents were purified by standard methods [32]. Chemicals were reagent grade. The phosphines PPh_2[2-(HOC)C_6H_4], $PPh_2(CH_2)_2Ph_2As$ (arphos), $Ph_2P(C_6H_4)O(C_6H_4)Ph_2P$ and Ph_2P[4-$(NMe_2)C_6H_4$] were purchased from Aldrich-Chemie. $Ph_2As(CH_2)_2Ph_2As$ (dppae) were purchased from ALFA. Microanalyses were carried out using a Carlo Erba Elemental Analyzer, Model 1108. The cyclometallated complexes **1a** and **1b** were synthesized using the procedure reported recently by us [21]. IR spectra were recorded as KBr discs on a Perkin–Elmer 1330 and on Mattson spectrophotometers. NMR spectra were obtained in $CDCl_3$ and referenced to $CHCl_3$ (^1H and $^{13}C–\{^1H\}$) or 85% H_3PO_4 ($^{31}P–\{^1H\}$) and were recorded on Bruker AC-2005 or Bruker AVANCE 300 spectrometers. All chemical shifts were reported downfield from standards. The FAB mass spectra were recorded using a Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix.

Analytical and spectroscopic data for the cyclometallated starting complexes **1a** and **1b**.

4.2. [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)C$_6$H$_4$]}]$_4$ (**1a**)

Anal. Calc. for $C_{64}H_{60}N_4O_{16}Pd_4$: C, 49.1; H, 3.8; N, 3.6. Found: C, 48.9; H, 3.8; N, 3.5%. IR: ν(C=N), 1589sh, m cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, δ ppm, *J* Hz): 3.51 [s, 3H, OMe]; 3.82 [s, 3H, OMe]; 4.02 [s, 3H, OMe]; 5.67 [s, 1H, H^5]; 7.57 [s, 1H, HC=N]; 6.62 [dd, 1H, H^8, $^3J(H^8H^9) = 7.6$, $^4J(H^8H^{10}) = 1.5$]; 6.37 [dt, 1H, H^9, $^3J(H^9H^{10}) = 7.5$, $^4J(H^9H^{11}) = 1.5$]; 6.91 [dt, 1H, H^{10}, $^3J(H^{10}H^{11}) = 7.5$, $^4J(H^8H^{10}) = 1.5$]; 7.44 [d, 1H, H^{11}, $^3J(H^{11}H^{10}) = 7.6$, $^4J(H^9H^{11}) = 1.5$]. FAB-MS: $m/z = 1566$ $[M]^+$; 391 $[M/4]^+$.

4.3. [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)-5-^{t}BuC$_6$H$_3$]}]$_4$ (**1b**)

Anal. Calc for $C_{68}H_{68}N_4O_{16}Pd_4$: C, 50.3; H, 4.2; N, 3.5. Found: C, 50.1; H, 4.1; N, 3.5%. IR: ν(C=N), 1571sh, m cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.24 [s, 9H, ^{t}Bu]; 3.38, 3.81, 4.03 [s, 9H, MeO]; 5.81 [s, 1H, H^5]; 6.75 [d, 1H, H^8, $^4J(H^8H^{10}) = 2.2$]; 6.99 [dd, 1H, H^{10}, $^3J(H^{10}H^{11}) = 8.8$, $^4J(H^8H^{10}) = 2.2$]; 7.35 [d, 1H, H^{11}]; 7.54 [s, 1H, HC=N]. FAB-MS: $m/z = 1792$ $[MH]^+$; 896 $[M/2]^+$.

4.4. [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)C$_6$H$_4$]}{PPh$_2$[2-(HOC)C$_6$H$_4$]}] (**2a**)

PPh_2(4-(HOC)C_6H_4) (49.8 mg, 0.31 mmol) was added to a suspension of [Pd{2,3,4-$(MeO)_3C_6HC(H)$=N(2-(O)-C_6H_4)] (36.9 mg, 0.31 mmol) in acetone (15 cm^3). The mixture was stirred for 12 h and the solvent removed to give a violet solid which was recrystallized from dichloromethane/hexane. Yield 56%. *Anal.* Calc. for $C_{35}H_{29}NO_5PPd$: C, 61.7; H, 4.3; N, 2.0. Found: C, 61.5; H, 4.3; N, 1.9%. IR: ν(C=O), 1697s cm^{-1}, ν(C=N), 1572s cm^{-1}. FAB-MS: $m/z = 680$ $[M]^+$. ^1H NMR (300 MHz, $CDCl_3$, δ ppm, *J* Hz): 10.37 [d, 1H, *H*C=O, $^4J(HP) = 2.4$], 8.14 [d, 1H, HC=N, $^4J(HP) = 10.8$], 7.59 [t, 1H,$^3J(HH) = 7.6$], 7.10 [d, 1H, H^8, $^3J(H^8H^9) = 7.1$], 6.89 [m, 2H, H^{10}, H^{11}], 6.30 [m, 2H, H^9, H^{11}], 5.54 [s, 1H, H^5, $^4J(H^5P) = 4.9$], 3.94 (s, 3H, MeO), 3.72 (s, 3H, MeO), 2.95 (s, 3H, MeO). $^{31}P–\{^1H\}$ NMR (121.44 MHz, $CDCl_3$, δ ppm): 33.3 s.

Compound **2b** was obtained following a similar procedure as a violet solid.

4.5. [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)-5-^{t}BuC$_6$H$_3$]}{PPh$_2$[2-(HOC)C$_6$H$_4$]}] (**2b**)

Yield 66%. *Anal.* Calc. for $C_{39}H_{38}NO_5PPd$: C, 63.4; H, 5.2; N, 1.9. Found: C, 63.4; H, 5.1; N, 1.8%. IR: ν(C=O), 1697s cm^{-1}, ν(C=N), 1571s cm^{-1}. FAB-MS: $m/z = 738$ $[M]^+$. ^1H NMR (200 MHz, $CDCl_3$, δ ppm, *J* Hz): 10.34 [d, 1H, *H*C=O, $^4J(HP) = 2.4$], 8.11 [d, 1H, HC=N, ^4J (HP) = 10.7], 7.02 [d, 1H, H^8, $^4J(H^8H^{10}) = 2.3$], 6.92 [dd, 1H, H^{10}, $^3J(H^{10}H^{11}) = 8.6$, $^4J(H^8H^{10}) = 2.3$], 6.22 [d, 1H, H^{11}, $^3J(H^{10}H^{11}) = 8.6$], 5.52 [s, 1H, H^5, $^4J(H^5P) = 3.9$], 3.98 (s, 3H, MeO), 3.74 (s, 3H, MeO), 2.95 (s, 3H, MeO), 1.24 (s, 9H, ^{t}Bu). $^{31}P–\{^1H\}$ NMR (80.96 MHz, $CDCl_3$, δ ppm) 33.3 s.

Compound **3a** was obtained following a similar procedure, as a red solid, but using a complex cyclometallated/diarsine 1:4 or 1:2 molar ratio.

4.6. [{Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)C$_6$H$_4$]}}$_2$-{μ-AsPh$_2$(CH$_2$)$_2$Ph$_2$As}] (**3a**)

Yield 49%, using 1:2 molar ratio and 21% using 1:4 molar ratio. *Anal.* Calc. for $C_{58}H_{54}N_2O_8Pd_2As_2$: C, 54.8;

H, 4.3; N, 2.2. Found: C, 54.7; H, 4.2; N, 2.1%. IR: ν(C=N), 1572s cm^{-1}.

FAB-MS: $m/z = 1271$ $[MH]^+$; 878, $[LPd(AsPh_2(CH_2)_2Ph_2As)]^+$. ^1H NMR (200 MHz, $CDCl_3$, δ ppm, J Hz): 7.57 [s, 1H, HC=N], 6.9 [m, 2H, H^8,H^{10}], 6.59 [d, 1H, H^{11}, $^3J(H^{10}H^{11}) = 7.8$], 6.35 [t, 1H, H^9, $J(H^8H^9) = 7.1$], 5.51 [s, 1H, H^5], 3.01 (s, br, 2H, $AsCH_2$), 3.93 (s, 3H, MeO), 3.71 (s, 3H, MeO), 2.63 (s, 3H, MeO).

Compounds **4a**, **4b** were prepared similarly, as violet solids, using a cyclometallated complex/arsinophosphine 1:4 molar ratio.

*4.7. [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)C$_6$H$_4$]}-{PPh$_2$(CH$_2$)$_2$Ph$_2$As-P}] (**4a**)*

Yield 64%. *Anal.* Calc. for $C_{42}H_{39}NO_4PPdAs$: C, 60.5; H, 4.7; N, 1.7. Found: C, 60.4; H, 4.6; N, 1.6%. IR: ν(C=N), 1569s cm^{-1}. FAB-MS: $m/z = 834$ $[MH]^+$. ^1H NMR (200 MHz, $CDCl_3$, δ ppm, J Hz): 8.15 [d, 1H, HC=N, $^4J(HP) = 9.7$], 7.13 [dd, 1H, H^8, $^3J(H^8H^9) = 8.0$, $^4J(H^8H^{10}) = 1.4$], 6.96 [dt, 1H, H^{10}, $^3J(H^9H^{10}) = 8.0$, $^4J(H^8H^{10}) = 1.4$], 6.63 [d, 1H, H^{11}, $^3J(H^{10}H^{11}) = 8.0$], 6.39 [t, 1H, H^9, $^3J(H^9H^{10}) = 8.0$], 5.47 [d, 1H, H^5, $^4J(H^5P) = 2.4$], 3.94 (s, 3H, MeO), 3.72 (s, 3H, MeO), 2.95 (s, 3H, MeO), 2.48 (br, 4H, PCH_2CH_2As). ^{31}P–{^1H} NMR (80.96 MHz, $CDCl_3$, δ ppm): 32.5 s.

*4.8. [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)-5-^{t}BuC$_6$H$_3$]}{PPh$_2$(CH$_2$)$_2$Ph$_2$As-P}] (**4b**)*

Yield 56%. *Anal.* Calc. for $C_{46}H_{47}NO_4PPdAs$: C, 62.1; H, 5.3; N, 1.6. Found: C, 62.2; H, 5.1; N, 1.5%. IR: ν(C=N), 1571s cm^{-1}. FAB-MS: $m/z = 890$ $[MH]^+$. ^1H NMR (200 MHz, $CDCl_3$, δ ppm, J Hz): 8.13 [d, 1H, H_i,$^4J(H_iP) = 10.2$], 7.08 [d, 1H, H^8, $^4J(H^8H^{10}) = 2.4$], 7.03 [dd, 1H, H^{10}, $^3J(H^{10}H^{11}) = 8.5$, $^4J(H^8H^{10}) = 2.4$], 6.57 [d, 1H, H^{11}, $^3J(H^{10}H^{11}) = 8.5$], 5.48 [s, 1H, H^5, $^4J(H^5P) = 3.4$], 3.97 (s, 3H, MeO), 3.72 (s, 3H, MeO), 2.95 (s, 3H, MeO), 2.47 (br, 4H, PCH_2CH_2As), 1.29 (s, 9H, ^{t}Bu). ^{31}P–{^1H} NMR (80.96 MHz, $CDCl_3$, δ ppm): 33.4 s.

Compound **5a** was obtained following a similar procedure as violet solid but using a complex cyclometallated/arphos 1:2 molar ratio.

*4.9. [{Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)C$_6$H$_4$]}}$_2$-{μ-PPh$_2$(CH$_2$)$_2$Ph$_2$As}] (**5a**)*

Yield 64%. *Anal.* Calc. for $C_{42}H_{39}NO_4PPdAs$: C, 60.5; H, 4.7; N, 1.7. Found: C, 60.4; H, 4.6; N, 1.6%. IR: ν(C=N), 1572s cm^{-1}. FAB-MS: $m/z = 1226$ $[M]^+$; 834 $[LPd(arphos)]^+$. ^1H NMR (200 MHz, $CDCl_3$, δ ppm, J Hz): 8.14 [d, 1H, HC=N, $^4J(HP) = 10.5$], 7.58 [s, 1H, H′C=N], 7.12 [d, br, 1H, H^8], 6.95 [t, br, 1H, H^{10}], 6.59 [dd, 1H, H^{11}, $^3J(H^{10}H^{11}) = 8.5$, $^4J(H^9H^{11}) = 2.4$], 6.38 [t, br, 1H, H^9], 5.56 [s, 1H, $H^{5\prime}$], 5.42 [d, 1H, H^5, $^4J(H^5P) = 3.9$], 3.95 (s, 6H, MeO), 3.71 (s, 6H, MeO), 2.84 (s, 3H, MeO), 2.81 (s, 3H, MeO), 3.01 (br, 4H, PCH_2CH_2As). ^{31}P–{^1H} NMR (80.96 MHz, $CDCl_3$, δ ppm): 34.0 s.

*4.10. [{Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)-^{t}BuC$_6$H$_3$]}}$_2${μ-PPh$_2$(C$_6$H$_4$)O(C$_6$H$_4$)Ph$_2$P}] (**6b**)*

A suspension of complex **1b** in acetone was treated with $PPh_2(C_6H_4)O(C_6H_4)Ph_2P$ (cyclometallated complex/diphosphine 1:4 or 1:2 molar ratio) in acetone and the resulting mixture was stirred for 24 h. The solvent was then removed under vacuum to give a violet solid which was chromatographed on a column packed with silica gel. Elution with CH_2Cl_2–C_2H_5OH (99:1) afforded a violet oil after solvent removal, which was recrystallized from dichloromethane–hexane to give the desired product as a violet solid. Yield 27%. *Anal.* Calc. for $C_{76}H_{74}N_2O_9P_2Pd_2$: C, 68.2; H, 5.2; N, 1.4. Found: C, 68.1; H, 5.1; N, 1.3%. IR: ν(C=N), 1565s cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): 8.00 [d, 1H, HC=N, $^4J(HP) = 10.7$], 5.59 [d, 1H, H^5, $^4J(H^5P) = 3.7$], 4.00 (s, 3H, MeO), 3.77 (s, 3H, MeO), 3.02 (s, 3H, MeO), 1.27 (s, 9H, ^{t}Bu). ^{31}P–{^1H} NMR (121.44 MHz, $CDCl_3$, δ ppm): 28.2 s.

Compound **7a** was obtained as a violet solid following a similar procedure to the one used for **6b** but using dichloromethane as solvent.

*4.11. [Pd{2,3,4-(MeO)$_3$C$_6$HC(H)=N[2-(O)C$_6$H$_4$]}-{PPh$_2$[4-(NMe$_2$)C$_6$H$_4$]}] (**7a**)*

Yield 67%, using 1:4 molar ratio, and 36% using 1:2 molar ratio. *Anal.* Calc. for $C_{36}H_{35}N_2PdO_4P$: C, 62.0; H, 5.1; N, 4.0. Found: C, 62.1; H, 5.1; N, 4.1%. IR: ν(C=N), 1572s cm^{-1}. FAB-MS: $m/z = 697$ $[M]^+$. ^1H NMR (300 MHz, $CDCl_3$, δ ppm, J Hz): 8.17 [d, 1H, HC=N, $^4J(HP) = 10.4$], 7.11 [dd, 1H, H^8, $^3J(H^8H^9) = 7.5$, $^4J(H^8H^{10}) = 1.9$], 6.89 [dt, 1H, H^{10}, $^3J(H^{10}H^{11}) = 8.4$, $^4J(H^8H^{10}) = 1.9$], 6.68 [dd, H^b, $^3J(H^aH^b) = 8.0$, $^4J(H^bP) = 1.6$], 6.44 [d, 1H, H^{11}, $^3J(H^{10}H^{11}) = 8.4$], 6.34 [t, 1H, H^9, $^3J(H^9H^{10}) = 7.5$], 5.61 [d, 1H, H^5, $^4J(H^5P) = 4.9$], 3.95 [s, 3H, MeO], 3.73 [s, 3H, MeO], 2.97 [s, 3H, MeO], 2.98 [s, 6H, Me_2]. ^{31}P–{^1H} NMR (121.44 MHz, $CDCl_3$, δ ppm): 32.3 s.

Acknowledgements

We thank the Ministerio de Educación y Ciencia (Project CTQ2006-15621-C02-01/BQU) for financial support.

References

[1] I. Omae, Organometallic Intramolecular-Coordination Compounds, Elsevier Science, Amsterdam New York, 1986.
[2] V.V. Dunina, O.A. Zalevskaya, V.M. Potapov, Russ. Chem. Rev. 571 (1984) 250.
[3] G.R. Newkome, W.E. Puckett, W.K. Gupta, G.E. Kiefer, Chem. Rev. 86 (1986) 451.
[4] A.D. Ryabov, Chem. Rev. 90 (1990) 403.
[5] M. Pfeffer, Recl. Trav. Chim. Pays-Bas 109 (1990) 567.

[6] J. Dupont, C.S. Consorti, J. Spencer, Chem. Rev. 105 (2005) 2527.
[7] V.V. Dunina, O.N. Gorunova, Russ. Chem. Rev. 73 (2004) 309.
[8] V.V. Dunina, O.N. Gorunova, Russ. Chem. Rev. 74 (2005) 871.
[9] (a) F.A. Cotton, B. Hong, Prog. Inorg. Chem. 40 (1992) 179;
(b) L.H. Pignolet, Homogeneous Catalysis with Metal Phosphine Complexes, Plenum Press, New York, 1983.
[10] T.J. Calcot, Chem. Rev. 103 (2003) 3101.
[11] (a) K.I. Na, S. Huh, K.M. Sung, M.J. Jun, Polyhedron 15 (1996) 1841;
(b) J.Y. Kim, M.J. Jun, W.Y. Lee, Polyhedron 15 (1996) 3787.
[12] M. Ito, M. Hirakawa, K. Murata, T. Ikariya, Organometallics 20 (2001) 379.
[13] G.P.C.M. Dekker, A. Buijs, C.J. Elseiver, K. Vrieze, P.W.N.M. van Leeuwen, W.J.J. Smeets, A.L. Spek, Y.F. Wang, C.H. Stam, Organometallics 11 (1992) 1937.
[14] A. Habtemariam, B. Watchman, B.S. Potter, R. Palmer, S. Parsons, A. Parkin, P.J. Sadler, J. Chem. Soc., Dalton Trans. (2001) 1306.
[15] A. Mansour, M. Portnoy, Tetrahedron Lett. 44 (2003) 2195.
[16] J.M. Vila, M. Gayoso, M.T. Pereira, A. Suárez, J.J. Fernández, J.M. Ortigueira, A. Fernández, M. López Torres, Trends Organometal. Chem. 2 (1997) 21.
[17] J.M. Vila, M.T. Pereira, J.M. Ortigueira, M. López-Torres, D. Lata, M. Graña, A. Suárez, J.J. Fernández, A. Fernández, J. Chem. Soc., Dalton Trans. (1999) 4193.
[18] D. Vázquez-García, A. Fernández, J.J. Fernández, M. López-Torres, A. Suárez, J.M. Ortigueira, J.M. Vila, H. Adams, J. Organomet. Chem. 595 (2000) 199.
[19] A.G. Quiroga, J.M. Perez, I. Lopez-Solera, J.R. Masaguer, A. Luque, P. Roman, A. Edwards, C. Alonso, C. Navarro-Ranninger, J. Med. Chem. 41 (1988) 1399.
[20] A. Amoedo, M. Graña, J. Martínez, T. Pereira, M. López-Torres, A. Fernández, J.J. Fernández, J.M. Vila, Eur. J. Inorg. Chem. (2002) 613.
[21] A. Fernández, D. Vázquez-García, J.J. Fernández, M. López-Torres, A. Suárez, S. Castro-Juiz, J.M. Vila, New J. Chem. 26 (2002) 105.
[22] C. López, A. Caubet, S. Pérez, X. Soláns, M. Font-Bardía, J. Organomet. Chem. 681 (2003) 82.
[23] J. Martínez, M.T. Pereira, I. Buceta, G. Alberdi, A. Amoedo, J.J. Fernández, M. López-Torres, J.M. Vila, Organometallics 22 (2003) 5581.
[24] H. Onoue, I. Moritani, J. Organomet. Chem. 43 (1972) 432.
[25] H. Onoue, K. Minami, K. Nakagawa, Bull. Chem. Soc. Jpn. 43 (1970) 3480.
[26] R. Bosque, J. Granell, J. Sales, M. Font-Bardiá, X. Solans, J. Organomet. Chem. 453 (1994) 147.
[27] J.M. Vila, M. Gayoso, M.T. Pereira, M. López-Torres, G. Alonso, J.J. Fernández, J. Organomet. Chem. 445 (1993) 287.
[28] 28 J.M. Vila, M. Gayoso, M.T. Pereira, A. Romar, J.J. Fernández, M. Thornton-Pett, J. Organomet. Chem. 401 (1991) 385.
[29] J. Albert, J. Granell, J. Sales, M. Font-Bardiá, X. Solans, Organometallics 14 (1995) 1393.
[30] P.S. Pregosini, R.W. Kuntz, ^{31}P and ^{13}C NMR of transition metal phosphine complexes, in: P. Diehl, E. Fluck, R. Kosfeld (Eds.), NMR Basic Principles and Progress, vol. 16, Springer, Berlin, 1979.
[31] D. Vázquez-García, A. Fernández, J.J. Fernández, M. López-Torres, A. Suárez, J.M. Ortigueira, J.M. Vila, H. Adams, J. Organomet. Chem. 595 (2000) 199.
[32] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, 4th ed., Butterworth–Heinemann, 1996.