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Cyclopalladated compounds derived from [C,N,O] terdentate ligands: synthesis, characterization and reactivity

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Abstract

Treatment of the Schiff base ligands 2-$ClC_6H_4C(H)=NCH_2(C_4H_7O)$ (**a**) and 3,4-$(MeO)_2C_6H_3C(H)=NCH_2(C_4H_7O)$ (**b**) with palladium(II) acetate in toluene or glacial acetic acid gave the dinuclear cyclometallated complexes $[Pd\{2\text{-}ClC_6H_3C(H)=NCH_2(C_4H_7O)\}(\mu\text{-}OAc)]_2$ (**1a**) and $[Pd\{3,4\text{-}(MeO)_2C_6H_2C(H)=NCH_2(C_4H_7O)\}(\mu\text{-}OAc)]_2$ (**1b**) with the ligand bonded to the palladium atom through the imine nitrogen and the C6 carbon atom. The ^1H and $^{13}C-\{^1H\}$ NMR spectra of the complexes show the occurrence in solution of three pairs of enantiomers. The acetato-bridged cyclometallated complex $[Pd\{3,4\text{-}(MeO)_2C_6H_2C(H)=NCH_2(C_4H_7O)\}(\mu\text{-}OAc)]_2$ (**1c**) was prepared from the enantiopure ligand (*R*)-3,4-$(MeO)_2C_6H_3(H)=NCH_2(C_4H_7O)$ (**c**). The NMR spectra of **1c** showed the existence of only two diastereomers in the solution. The reaction of **1a** and **1b** with aqueous sodium chloride gave the chloro-bridged complexes $[Pd\{2\text{-}ClC_6H_3C(H)=NCH_2(C_4H_7O)\}(\mu\text{-}Cl)]_2$ (**2a**) and $[Pd\{3,4\text{-}(MeO)_2C_6H_2C(H)=NCH_2(C_4H_7O)\}(\mu\text{-}Cl)]_2$ (**2b**) after a metathesis reaction. The reaction of **2a** with PPh_3 in acetone gave the mononuclear cyclometallated complex $[Pd\{2\text{-}ClC_6H_3C(H)=NCH_2(C_4H_7O)\}(Cl)(PPh_3)]$ (**3a**) in a bridge-splitting reaction. Treatment of **3a** with silver triflate gave the cyclometallated complex $[Pd\{2\text{-}ClC_6H_3C(H)=NCH_2(C_4H_7O)\}(PPh_3)][CF_3SO_3]$ (**4a**) in which the palladium atom is bonded to four different atoms C, N, O and P. When complex **2a** was reacted with silver triflate in acetone complex $[Pd\{2\text{-}ClC_6H_3C(H)=NCH_2(C_4H_7O)\}((CH_3)_2CO)][CF_3SO_3]$ (**5a**) was obtained with the ligand as [C,N,O] coordinated. The reaction of complexes **2a** and **2b** with the diphosphine dppp in a complex–phosphine 1:1 molar ratio gave the dinuclear cyclometallated complexes $[\{Pd[2\text{-}ClC_6H_3C(H)=NCH_2(C_4H_7O)](Cl)\}_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2)]$ (**8a**) and $[\{Pd[3,4\text{-}(MeO)_2C_6H_2C(H)=NCH_2(C_4H_7O)](Cl)\}_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2)]$ (**5b**) with the diphosphine bridging the two palladium atoms. Reaction of complexes **2a** and **2b** with the phosphines dppp and *cis*-dppe in a 1:2 molar ratio gave the mononuclear complexes $[Pd\{2\text{-}ClC_6H_3C(H)=NCH_2(C_4H_7O)\}\{Ph_2P(CH_2)_3Ph_2\text{-}P,P\}][ClO_4]$ (**6a**), $[Pd\{3,4\text{-}(MeO)_2C_6H_2C(H)=NCH_2(C_4H_7O)\}\{Ph_2P(CH_2)_3Ph_2\text{-}P,P\}][ClO_4]$ (**3b**) and $[Pd\{2\text{-}ClC_6H_2C(H)=NCH_2(C_4H_7O)\}(cis\text{-}Ph_2PCH=CHPh_2\text{-}P,P)][Cl]$ (**4b**). The treatment of **2a** with the triphosphine bis(2-diphenylphosphinoethyl)phenylphosphine in 1:2 molar ratio, followed by treatment with sodium perchlorate gave $[Pd\{3,4\text{-}(MeO)_2ClC_6H_3C(H)=NCH_2(C_4H_7O)\}\{(PPh_2CH_2CH_2)_2PPh\text{-}P,P,P\}][ClO_4]$ (**7a**) in which the palladium atom is bonded to the triphosphine through the three phosphorus atoms and to the Schiff base ligand through one carbon atom and the imine nitrogen.

Keywords: C–H activation; Cyclometallation; Phosphorus ligands; Schiff bases; Palladium

1. Introduction

The study of cyclometallated compounds has attracted much attention over the last three decades [1–5]. They present numerous applications in organic and organometallic synthesis [6], in insertion reactions [7], in optical resolution [8], in the determination of the enantiomeric excess [9], in the synthesis of new metal mesogenic compounds [10], biologically active compounds [11,12], in catalytic materials [13], in the building of new self assembly supramolecular species [14], and to promote unusual coordination environments [15].

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Our interest in cyclometallated complexes has been, in part, focused on the study of compounds derived from potentially [C,N,X] (X = O, S, N) terdentate ligands, such as semicarbazones [16,17], thiosemicarbazones [18,19] or Schiff bases [20–23] which react with palladium(II) and platinum(II) or palladium(0) to give cyclometallated complexes with two fused rings at the metal. In spite of the large number of [C,N,N] derivatives reported [24], relatively few [C,N,O] derivatives are known [25].

Semicarbazones are known to react readily with $M_2[PdCl_4]$ (M = Li, K) to give mononuclear cyclometallated complexes; however, complexes derived from thiosemicarbazones show tetranuclear structures.

In the present paper we report the synthesis of new cyclometallated compounds derived from the potentially terdentate Schiff bases 2-$ClC_6H_4C(H)$=NCH_2-(C_4H_7O) (**a**) and 3,4-$(MeO)_2C_6H_3C(H)$=$NCH_2(C_4H_7O)$ (**b**). We have found that direct reaction with Pd(II) or Pd(0) salts did not yield the expected complex with the ligand in a [C,N,O] terdentate fashion. Thus, in an oxidative addition reaction, treatment of **a** with $[Pd_2(dba)_3]$, in benzene under reflux, gave an untreatable mixture which was not further investigated, and reaction of **a** or **b** with palladium(II) acetate, in glacial acetic acid, only yielded the dimeric acetato-bridged complexes **1a** and **1b** with the corresponding ligand as [C,N] bidentate. However, the vacant site produced in the coordination sphere of the palladium atom, upon reaction of the cyclometallated halogen-bridged dimer complexes with a Ag(I) salt, promotes formation of the Pd–O bond. The reactivity of the cyclometallated complexes with mono-, di- and triphosphines is reported, and we also describe a new type of stereoisomerism arising from the folded open-book disposition of the cyclometallated ligands in the acetato-bridged dimers **1a** and **1b**.

2. Experimental

Safety note: Caution: perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and handled with great caution.

2.1. General procedures

Solvents were purified by standard methods [26]. Chemicals were reagent grade. The phosphines PPh_3, *cis*-Ph_2PCH=$CHPPh_2$ (*cis*-dppe), $Ph_2P(CH_2)_3PPh_2$ (dppp) and $(Ph_2PCH_2CH_2)_2PPh$ (triphos) were purchased from Aldrich-Chemie. Microanalyses were carried out using a Carlo–Erba elemental analyzer, model 1108. IR spectra were recorded as Nujol mulls or KBr discs on a Perkin–Elmer 1330 and on a Mattson spectrophotometers. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H, $^{13}C-\{^1H\}$) or 85% H_3PO_4 ($^{31}P-\{^1H\}$) and were recorded on a Bruker AC-2005 spectrometer. 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. Conductivity measurements were made on a CRISON GLP 32 conductivimeter using 10^{-3} mol dm^{-3} solutions in dry acetonitrile.

The syntheses of 2-$ClC_6H_4C(H)$=$NCH_2(C_4H_7O)$ (**a**) and 3,4-$(MeO)_2C_6H_3C(H)$=$NCH_2(C_4H_7O)$ (**b**) were performed by heating chloroform solutions of the appropriate quantities of tetrahydrofurfurylamine and 2-chlorobenzaldehyde or 3,4-dimethoxybenzaldehyde, respectively, in a Dean–Stark apparatus under reflux. Schiff base ligand (*R*)-3,4-$(MeO)_2C_6H_3C(H)$=NCH_2-(C_4H_7O) (**c**) was prepared similarly using enantiopure (*R*)-tetrahydrofufurylamine. IR (ν_{max}/cm^{-1}) (C=N) 1640s (**a**), 1645s (**b**, **c**). $^{13}C-\{^1H\}$ NMR for ligand **a**: (50.28 MHz, $CDCl_3$): δ 158.9 (C=N); δ 135.0 (C1); δ 129.6 (C6); δ 131.1 (C2); δ 126.8 (C5); δ 128.3, 131.4 (C3, C4); δ 78.3 (C8); δ 68.1 (C11); δ 65.8 (C7); δ 29.2, 25.7 (C9, C10). $^{13}C-\{^1H\}$ NMR for ligand **b, c**: δ 161.9 (C=N); δ 151.3, 149.2 (C3, C4); δ 129.4 (C1); δ 123.1 (C6); δ 110.3, 108.8 (C2, C5); δ 78.5 (C8); δ 68.1 (C11); δ 65.7 (C7); δ 29.3, 25.6 (C9, C10); δ 55.8 (OCH_3).

2.2. Syntheses

2.2.1. *[Pd{2-$ClC_6H_3C(H)$=$NCH_2(C_4H_7O)$}(μ-OAc)]$_2$ (1a)*

A pressure tube containing 2-$ClC_6H_4C(H)$=NCH_2-(C_4H_7O) (**a**) (150 mg, 0.67 mmol), palladium(II) acetate (150 mg, 0.67 mmol) and 25 cm^3 of dry toluene was sealed under argon. The resulting mixture was heated at 60 °C for 3 h. After cooling to room temperature (r.t.) the orange precipitate formed was filtered off and dissolved in chloroform. The red solution obtained was filtered through Celite to remove the black palladium formed. The solvent was removed under vacuum to give an orange solid which was chromatographed on a column packed with silica gel. Elution with dichloromethane–methanol (1%) afforded the final product after concentration. Yield 44%. *Anal.* Found: C, 43.2; H, 4.2; N, 3.6. Calc. for $C_{28}H_{32}N_2O_6Cl_2Pd_2$: C, 43.3; H, 4.1; N, 3.6%. IR: ν(C=N), 1610s cm^{-1}; ν_{as}(COO), 1560s cm^{-1}; ν_s(COO), 1410s cm^{-1}. $^{13}C-\{^1H\}$ NMR: (50.28 MHz, $CDCl_3$): δ 171.6, 171.7 (C=N); δ 156.9, 156.7 (C6); δ 143.2, 143.0 (C1); δ 131.0 (C2); δ 124.6, 124.7 (C5); δ 130.1, 130.2, 130.3, 130.4 (C3, C4); δ 76.6 (C8); δ 68.5 (C11); δ 63.6, 61.6 (C7); δ 29.1, 28.4, 25.9, 25.5 (C9, C10); δ 173.0 (CH_3COO); δ 24.4 (CH_3COO). FAB MS: m/z = 776 $[M]^+$; 717 $[M-AcO]^+$.

Complexes **1b** and **1c** were prepared similarly.

*2.2.2. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$-(C$_4$H$_7$O)}(μ-OAc)]$_2$ (**1b**)*

Yield 56%. *Anal*. Found: C, 46.2; H, 5.2; N, 3.3. Calc. for $C_{32}H_{42}N_2O_{10}Pd_2$: C, 46.4; H, 5.1; N, 3.4%. IR: ν(C=N), 1608m cm^{-1}; ν_{as}(COO), 1570s cm^{-1}; ν_s(COO), 1415s cm^{-1}. ^{13}C–{^{1}H} NMR: (50.28 MHz, $CDCl_3$): δ 173.8, 173.7, 172.5, 172.4 (C=N); δ 149.3, 149.0 (C6); δ 149.4, 146.0 (C3, C4); δ 137.8, 137.4 (C1); δ 114.1, 109.9 (C2, C5); δ 76.9 (C8); δ 68.3, 67.8 (C11); δ 62.7, 60.1 (C7); δ 29.1, 28.6, 25.8, 25.4 (C9, C10); δ 181.1, 180.0 (CH_3COO); δ 24.4, 24.3 (CH_3COO); δ 56.2, 55.7 (OCH_3).

*2.2.3. (R)-[Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$-(C$_4$H$_7$O)}(μ-OAc)]$_2$ (**1c**)*

Yield 65%. *Anal*. Found: C, 45.7; H, 5.4; N, 3.2. Calc. for $C_{32}H_{42}N_2O_{10}Pd_2$: C, 46.4; H, 5.1; N, 3.4%. IR: ν(C=N), 1608m cm^{-1}; ν_{as}(COO), 1570s cm^{-1}; ν_s(COO), 1415s cm^{-1}. ^{13}C–{^{1}H} NMR: (50.28 MHz, $CDCl_3$): δ 173.8, 172.4 (C=N); δ 149.3 (C6); δ 149.4, 146.0 (C3, C4); δ 137.8, 137.4 (C1); δ 114.1, 109.9 (C2, C5); δ 76.9 (C8); δ 68.3, 67.8 (C11); δ 62.7, 60.1 (C7); δ 29.1, 28.6, 25.8, 25.4 (C9, C10); δ 181.1, 180.0 (CH_3COO); δ 24.4, 24.3 (CH_3COO); δ 56.2, 55.7 (OCH_3).

*2.2.4. [Pd{2-ClC$_6$H$_3$C(H)=NCH$_2$(C$_4$H$_7$O)}(μ-Cl)]$_2$ (**2a**)*

An aqueous solution of NaCl (ca. 10^{-2} M) was added dropwise to a solution of **1a** (200.0 mg, 0.257 mmol) in 10 cm^3 of acetone. The resulting mixture was stirred for 6 h. The yellow precipitate formed was filtered off, washed with water and dried under vacuum. Yield 86%. *Anal*. Found: C, 39.9; H, 3.3; N, 3.7. Calc. for $C_{24}H_{26}N_2O_2Cl_4Pd_2$: C, 39.5; H, 3.6, N, 3.8%. IR: ν(C=N), 1615s cm^{-1}. ^{13}C–{^{1}H} NMR: (50.28 MHz, $CDCl_3$): δ 174.4 (C=N); δ 155.2 (C6); δ 143.3 (C1); δ 131.1 (C2); δ 125.4 (C5); δ 131.3, 131.7 (C3, C4); δ 76.7 (C8); δ 68.2 (C11); δ 63.7 (C7); δ 28.9, 25.8 (C9, C10). FAB MS: $m/z = 765$ $[M + Cl]^+$; 693 $[M - Cl]^+$.

Complex **2b** was prepared similarly as a yellow solid.

*2.2.5. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$-(C$_4$H$_7$O)}(μ-Cl)]$_2$ (**2b**)*

Yield 91%. *Anal*. Found: C, 43.4; H, 4.3; N, 3.7. Calc. for $C_{28}H_{36}N_2O_6Cl_2Pd_2$: C, 43.1; H, 4.6, N, 3.6%. IR: ν(C=N), 1610m cm^{-1}. FAB MS: $m/z = 780$ $[M]^+$; 745 $[M - Cl]^+$.

*2.2.6. [Pd{2-ClC$_6$H$_3$C(H)=NCH$_2$(C$_4$H$_7$O)}(Cl)(PPh$_3$)] (**3a**)*

PPh_3 (22.0 mg, 0.082 mmol) was added to a suspension of **2a** (30.0 mg, 0.041 mmol) in acetone (15 cm^3). The mixture was stirred for 12 h and the white precipitate formed filtered off, dried under vacuum and recrystallized from chloroform–hexane. Yield 74%. *Anal*. Found: C, 57.1; H, 4.9; N, 2.3. Calc. for $C_{30}H_{28}NOCl_2PdP$: C, 57.5; H, 4.5; N, 2.2%. IR: ν(C=N), 1620m cm^{-1}. ^{13}C–{^{1}H} NMR: (50.28 MHz, $CDCl_3$): δ 175.0 (d, C=N, $JPC = 4.2$ Hz); δ 160.0 (C6); δ 145.0 (C1); δ 131.3 (C2); δ 124.8 (C5); δ 131.0, 131.9 (C3, C4); δ 77.5 (C8); δ 67.9 (C11); δ 65.6 (C7); δ 28.8, 25.8 (C9, C10). P-phenyl: δ 135.4 (d, C_o, $JPC = 12.1$ Hz); δ 128.0 (d, C_m, $JPC = 11.3$ Hz); δ 130.8 (d, C_p, $JPC = 2.8$ Hz); δ 130.7 (d, C_i, $JPC = 42.5$ Hz). FAB MS: $m/z = 627$ $[M]^+$; 590 $[M - Cl]^+$.

*2.2.7. [Pd{2-ClC$_6$H$_3$C(H)=NCH$_2$(C$_4$H$_7$O)}-(PPh$_3$)][CF$_3$SO$_3$] (**4a**)*

A suspension of **3a** (24.0 mg, 0.020 mmol) in acetone (15 cm^3) was treated with silver trifluoromethanesulfonate (5.2 mg, 0.020 mmol) and stirred for 24 h. The resulting solution was filtered through Celite to eliminate the AgCl precipitate and the solvent removed to give a yellow solid, which was recrystallized from chloroform–hexane. Yield 60%. *Anal*. Found: C, 50.1; H, 3.7; N, 2.1. Calc. for $C_{31}H_{28}NO_4F_3ClSPdP$: C, 50.3; H, 3.8; N, 1.9%. IR: ν(C=N), 1620m cm^{-1}. ^{13}C–{^{1}H} NMR: (50.28 MHz, $CDCl_3$): δ 173.6 (d, C=N, $JPC = 3.5$ Hz); δ 151.3 (C6); δ 145.5 (C1); δ 127.7 (C2); δ 126.3 (C5); δ 128.7 (C3, C4); δ 81.9 (C8); δ 69.7 (C11); δ 61.7 (C7); δ 28.4 (C9, C10). P-phenyl: δ 134.9 (d, C_o, $JPC = 12.1$ Hz); δ 129.0 (d, C_m, $JPC = 10.6$ Hz); δ 131.8 (d, C_p, $JPC = 2.8$ Hz); δ 132.4 (d, C_i, $JPC = 48.2$ Hz). FAB MS: $m/z = 592$ $[M - CF_3SO_3]^+$. Specific molar conductivity, $\Lambda_m = 156.4$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

*2.2.8. [{Pd[2-ClC$_6$H$_3$C(H)=NCH$_2$(C$_4$H$_7$O)](Cl)}$_2$-(μ-Ph$_2$P(CH$_2$)$_3$PPh$_2$)] (**8a**)*

$Ph_2P(CH_2)_3PPh_2$ (dppp) (17.0 mg, 0.041 mmol) was added to a suspension of **2a** (30.0 mg, 0.041 mmol) in acetone (15 cm^3). The mixture was stirred for 12 h and the precipitate formed filtered off and dried under vacuum to give a white solid which was recrystallized from chloroform–hexane. Yield 51%. *Anal*. Found: C, 49.1; H, 4.3; N, 2.3. Calc. for $C_{51}H_{52}N_2O_2Cl_4Pd_2P_2.CHCl_3$: C, 49.5; H, 4.2; N, 2.2%. IR: ν(C=N), 1623m cm^{-1}.

Compound **5b** was prepared similarly as a white solid.

*2.2.9. [{Pd[3,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$-(C$_4$H$_7$O)](Cl)}$_2$(μ-Ph$_2$P(CH$_2$)$_3$PPh$_2$)] (**5b**)*

Yield 55%. *Anal*. Found: C, 55.1; H, 5.0; N, 2.3. Calc. for $C_{55}H_{62}N_2O_6Cl_2Pd_2P_2$: C, 55.4; H, 5.2; N, 2.3%. IR: ν(C=N), 1615m cm^{-1}.

*2.2.10. [Pd{2-ClC$_6$H$_3$C(H)=NCH$_2$(C$_4$H$_7$O)}-(Ph$_2$P(CH$_2$)$_3$Ph$_2$–P,P)][ClO$_4$] (**6a**)*

$Ph_2P(CH_2)_3Ph_2$ (dppp) (34.0 mg, 0.082 mmol) was added to a suspension of **2a** (30.0 mg, 0.041 mmol) in

acetone (20 cm^3). The mixture was stirred for 1 h, after which an excess of sodium perchlorate was added. The complex was then precipitated out by addition of water, filtered off and dried in vacuo. Recrystallization from chloroform–hexane gave the final compound as a white solid. Yield 85%. *Anal*. Found: C, 55.1; H, 4.2; N, 3.0. Calc. for $C_{39}H_{39}N_2O_5Cl_2P_2Pd$: C, 54.8; H, 4.6; N, 3.3%. IR: ν(C=N), 1617m cm^{-1}. Specific molar conductivity, $\Lambda_m = 113.5$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

Complex **3b** was synthesized similarly as a yellow solid.

2.2.11. [Pd{3,4-(MeO)$_2$C$_6$H$_3$C(H)=NCH$_2$(C$_4$H$_7$O)}-(Ph$_2$P(CH$_2$)$_3$Ph$_2$–P,P)][ClO$_4$] (3b)

Yield 85%. *Anal*. Found: C, 56.1; H, 5.0; N, 1.9. Calc. for $C_{41}H_{44}NO_7ClPdP_2$: C, 56.8; H, 5.1; N, 1.6%. IR: ν(C=N), 1615m cm^{-1}. Specific molar conductivity, $\Lambda_m = 140.3$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

2.2.12. [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$(C$_4$H$_7$O)}-(cis-Ph$_2$PCH=CHPh$_2$–P,P)][Cl] (4b)

cis-$Ph_2PCH{=}CHPh_2$ (*cis*-dppe) (30.0 mg, 0.074 mmol) was added to a suspension of **2b** (29.0 mg, 0.037 mmol) in acetone (20 cm^3). The mixture was stirred for 1 h. The complex was then precipitated out by addition of water, filtered off and dried in vacuo. Recrystallization from chloroform–hexane gave the final compound as a white solid. Yield 62%. *Anal*. Found: C, 48.8; H, 4.5; N, 2.0. Calc. for $C_{40}H_{40}NO_3ClP_2Pd{\cdot}2CHCl_3$: C, 49.2; H, 4.1; N, 1.4%. IR: ν(C=N), 1606m cm^{-1}. Specific molar conductivity, $\Lambda_m = 90.3$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

Complex **7a** was synthesized as a yellow solid using a similar procedure to the one described for complex **6a**.

2.2.13. [Pd{2-ClC$_6$H$_3$C(H)=NCH$_2$(C$_4$H$_7$O)}-{(PPh$_2$CH$_2$CH$_2$)$_2$PPh–P,P,P}][ClO$_4$] (7a)

Yield 95%. *Anal*. Found: C, 52.0; H, 4.5; N, 1.5. Calc. for $C_{46}H_{46}NO_5Cl_2P_3Pd{\cdot}CHCl_3$: C, 52.1; H, 4.4; N, 1.3%. IR: ν(C=N), 1615m cm^{-1}. $^{13}C-\{^1H\}$ NMR: (50.28 MHz, $CDCl_3$): δ 168.8 (d, C=N, $JPC = 5.0$); δ 139.6 (C1); δ 135.4 (C2); δ 124.5 (C5); δ 77.7 (C8); δ 67.9 (C11); δ 63.1 (C7); δ 28.8, 25.8 (C9, C10). FAB MS: $m/z = 862.2$ $[M - ClO_4]^+$. Specific molar conductivity, $\Lambda_m = 146.3$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

2.2.14. [Pd{2-ClC$_6$H$_3$C(H)=NCH$_2$(C$_4$H$_7$O)}-((CH$_3$)$_2$CO)][CF$_3$SO$_3$] (5a)

A suspension of **2a** (30.0 mg, 0.041 mmol) in acetone (8 cm^3) was treated with silver trifluoromethanesulfonate (22.0 mg, 0.082 mmol) and stirred for 24 h. The resulting solution was filtered through Celite to eliminate the AgCl precipitate and the solvent removed to give a hygroscopic yellow solid which was recrystallized from dichloromethane–hexane and stored under nitrogen. Yield 65%. *Anal*. Found: C, 36.1; H, 3.3; N, 2.1. Calc. for $C_{16}H_{19}NO_5F_3ClSPd$: C, 35.8; H, 3.6; N, 2.6%. IR: ν(C=N), 1608m cm^{-1}. $^{13}C-\{^1H\}$ NMR: (50.28 MHz, $CDCl_3$): δ 174.1 (C=N); δ 151.3 (C6); δ 143.3 (C1); δ 131.4 (C2); δ 126.1 (C5); δ 132.0, 129.8 (C3, C4); δ 79.6 (C8); δ 70.1 (C11); δ 62.4 (C7); δ 28.5, 25.6 (C9, C10); δ 31.2, 29.7 ($CH_3C{=}O$). Specific molar conductivity, $\Lambda_m = 240.2$ ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

3. Results and discussion

For the convenience of the reader the compounds and reactions are shown in Scheme 1. The compounds described in this paper were characterized by elemental analysis (C, H, N) and by IR spectroscopy (data in Section 2) and by ^1H, $^{31}P-\{^1H\}$ (see Table 1) and, in part, $^{13}C-\{^1H\}$ NMR spectroscopy and FAB mass spectrometry (Section 2).

Reaction of the Schiff base ligands 2-$ClC_6H_4C(H){=}NCH_2(C_4H_7O)$ (**a**) and 3,4-$(MeO)_2C_6H_3C(H){=}NCH_2(C_4H_7O)$ (**b**) with palladium(II) acetate in toluene gave the dinuclear cyclometallated complexes [Pd{2-$ClC_6H_3C(H){=}NCH_2(C_4H_7O)$}(μ-OAc)]$_2$ (**1a**) and [Pd{3,4 - $(MeO)_2C_6H_2C(H){=}NCH_2(C_4H_7O)$}(μ - OAc)]$_2$ (**1b**), respectively, which were fully characterized. The IR spectra of **1a** and **1b** showed the ν(C=N) stretch at 1610 and 1608 cm^{-1}, respectively, shifted to lower wavenumbers (as compared to the free ligand) due to N-coordination of the imine [27,28]. The IR spectra also showed strong bands assigned to the symmetric and asymmetric ν(COO) vibrations, in agreement with those expected for bridging acetate ligands [29] (see Section 2). The resonance corresponding to the HC=N proton in the ^1H NMR spectra was shifted to lower frequency consequent upon coordination of the imine group to the palladium atom *via* the lone pair of the nitrogen atom [30]. The assignment of the aromatic proton resonances unequivocally showed that metallation had taken place at the C6 carbon atom for both compounds (see Table 1).

A noticeable feature of the ^1H NMR spectra of **1a** and **1b** is the number of signals for the HC=N and aromatic protons. Four singlets for the HC=N protons were assigned in each case. For complex **1a** a multiplet was assigned to the H^3, H^4 and H^5 resonances, whereas for complex **1b** two singlets were assigned to each one of the H^2 and H^5 protons. We reasoned that the splitting could be caused by the presence of the *syn* and *anti* conformations, as acetato-bridged dimers exist in a folded arrangement which gives rise to two isomers: the *anti* isomer with C_2 symmetry and the *syn* isomer with C_s symmetry (see Fig. 1). By far, the *anti* disposition is the most frequent [31].

If both isomers were present two resonances would be expected for the HC=N protons and three for the

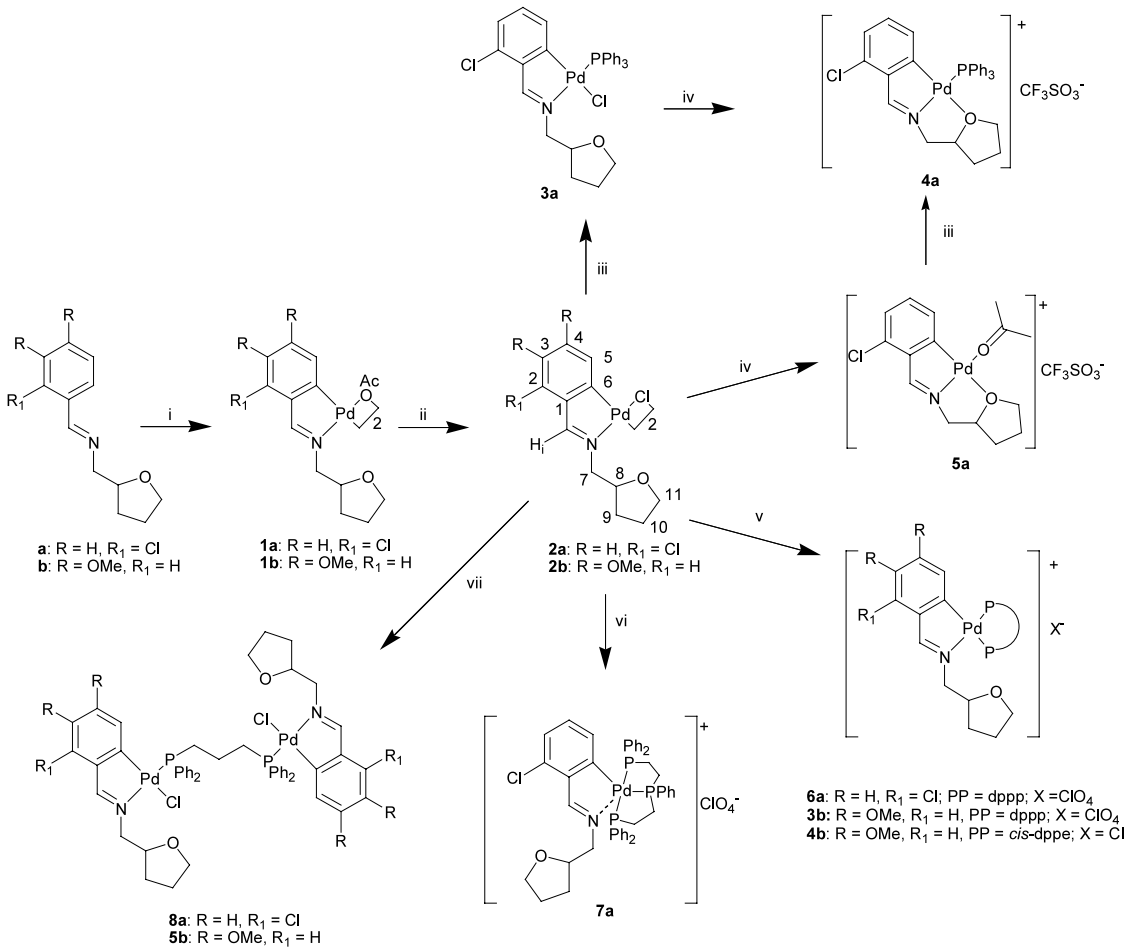
acetate MeCOO protons (one for the *anti* isomer and two for the *syn* separated by approximately 0.2 ppm [32]). However in the ^{1}H NMR spectra of **1a** and **1b** only two resonances, separated by approximately 0.02 ppm, were assignable to the acetate methyl groups.

Therefore, we believe that the number of signals found may be due to the presence of several diastereoisomers in solution.

Because the syntheses of ligands **a** and **b** were performed by heating a chloroform solution of (*R*,*S*)-tetrahydrofurfurylamine with 2-chlorobenzaldehyde or 3,4-dimethoxybenzaldehyde, as appropriate, the ligands would in fact be equimolar mixtures of both enantiomers and the cyclopalladated compounds **1a** and **1b** would yield a mixture of three pairs of enantiomers (see Fig. 2).

The NMR spectra of each pair of enantiomers are identical, but obviously different from those of their correspondent diastereoisomers. One set of signals is expected for enantiomers **I** and **II**, and another set for enantiomers **III** and **IV**; however, **V** and **VI** should give two groups of resonances for the protons of each cyclometallated unit of the acetate dimer. Thus, four signals could be assigned to the HC=N protons in the ^{1}H NMR spectra of the complexes, two resonances for the aromatic protons and two for the acetate methyl protons. The intensities of the signals for **V** and **VI** are the same as those for the **I**–**IV** enantiomers. Due to their similar solubility we were not able to separate the three pairs of enantiomers. Surprisingly, none of the other derivatives of ligands **a** and **b** showed splitting of the NMR signals. We attribute these findings to the folded structure of the acetato-bridged complex which brings close together the cyclometallated units. The asymmetric C8 carbon atom of one unit is situated close to the neighboring cyclometallated ligand, thus experiencing a different chemical environment in each diastereomer. Since the folded structure brings the HC=N proton close to the C8 carbon, the chemical differences between the diastereoisomers are most evident in the HC=N resonances.

In order to confirm this we synthesized the enantiopure ligand **c** by reaction of (*R*)-tetrahydrofufurylamine with 3,4-dimethoxybenzaldehyde. The ^{1}H NMR spectra



Scheme 1. (i) $Pd(AcO)_2$ (toluene or acetic acid); (ii) NaCl (acetone/water); (iii) PPh_3 (acetone); (iv) $AgCF_3SO_3$ (acetone); (v) dppp, $NaClO_4$ or *cis*-dppe (acetone, 1:2 molar ratio); (vi) triphos (acetone 1:2 molar ratio); (vii) dppp (acetone, 1:1 molar ratio).

Table 1
^{31}P and ^{1}H NMR

Compound	^{31}P	Aromatic	Others
a		8.03[d, 1H, H^6, 5.86 [a]] 7.3[m, 3H, H^3, H^4, H^5]	8.71[s, 1H, H_i] 4.21[m, 1H, H^8] 3.65[m, 4H, H^7, H^{11}] 1.8[m, 4H, H^9, H^{10}]
1a [b]		6.9[m, 6H, H^3, H^4, H^5]	7.76, 7.73, 7.69, 7.64 [s, 2H, H_i] 4.30[m, 2H, H^8] 3.75[m, 4H, H^{11}] 4.04[m, 2H, H^7] 3.30[m, 2H, H^7] 1.9[m, 8H, H^9, H^{10}]
2a		7.23[m, 2H, H^3] 6.97[m, 4H, H^4, H^5]	8.21[s, 2H, H_i] 4.41[m, 2H, H^8] 3.46[m, 2H, H^7] 3.85[m, 6H, H^7, H^{11}] 1.93[m, 8H, H^9, H^{10}]
3a	43.0s	6.82[d, 1H, H^3, 7.3 [a]] 6.43[t, 1H, H^4, 7.3 [a]] 6.25[dd, 1H, H^5, 6.4 [d]]	8.62[d, 1H, H_i, 8.3 [d]] 4.60[m, 2H, H^7, H^8] 3.40[m, 1H, H^7] 3.87[m, 2H, H^{11}] 1.90[m, 4H, H^9, H^{10}]
4a	39.60s	6.93[dd, 1H, H^3, 7.8 [a], 0.98 [c]] 6.51[t, 1H, H^4, 7.8 [a]] 6.23[m, 1H, H^5, 5.9 [d]]	8.62[d, 2H, H_i, 7.8 [d]] 4.40[m, 1H, H^8] 4.05, 3.90, 3.72 [m, 3H, H^7, H^{11}] 3.36[m, 1H, H^7] 2.3–1.7 [m, 4H, H^9, H^{10}]
5a [e]		6.98, 6.92 [m, 3H, H^3, H^4, H^5]	8.07[s, 1H, H_i] 4.40[m, 1H, H^8] 4.05, 3.90, 3.80 [m, 3H, H^7, H^{11}] 3.49[m, 1H, H^7] 2.0 [m, 4H, H^9, H^{10}]
6a	25.2d, −2.9d, 58.2 [f]	6.86[d, 1H, H^3, 7.4 [a]] 6.40m[s, 1H, H^4, H^5]	8.74[d, 1H, H_i, 7.0 [d]] 4.50[m, 1H, H^8] 3.7[m, 4H, H^7, H^{11}] 1.90[m, 4H, H^9, H^{10}]
7a	89.3t, 45.4d, 27.1 [f]	6.91[d, 1H, H^3, 7.8 [a]] 6.36[dd, 1H, H^4, 7.8 [a], 0.98 [c]] 5.76[t, 1H, H^5, 7.8 [d]]	8.37[s, 1H, H_i] 3.48, 3.24 [m, 5H, H^8, H^7, H^{11}]
8a	33.3s	6.80[d, 1H, H^3, 7.8 [a]] 6.46[t, 1H, H^4, 7.8 [a]] 6.22[dd, 1H, H^5, 5.9 [d]]	8.52[d, 1H, H_i, 7.8 [d]] 4.47[m, 2H, H^7, H^8] 3.52[m, 1H, H^7] 3.87[m, 2H, H^{11}] 2.10–1.70[m, 4H, H^9, H^{10}]
b, **c**		7.34[d, 1H, H^2, 1.9 [c]] 7.06[dd, 1H, H^5, 8.3 [a]] 7.76[d, 1H, H^6]	8.10[s, 1H, H_i] 4.20[m, 1H, H^8] 3.65, 3.55 [m, 4H, H^7, H^{11}] 1.9[m, 8H, H^9, H^{10}] 3.83, 3.79[s, 6H, OMe]
1b[b]		6.71, 6.69, 6.55, 6.53[s, 4H, H^2, H^5]	7.43, 7.42, 7.33, 7.29[s, 2H, H_i] 4.29[m, 2H, H^8] 1.9[m, 8H, H^9, H^{10}] 3.86, 3.79[s, 12H, OMe]
2b		6.80, 6.89[2, 4H, H^2, H^5]	7.75[s, 2H, H_i] 4.38[m, 2H, H^8] 3.46[m, 2H, H^7] 3.80[m, 6H, H^7, H^{11}] 1.92[m, 8H, H^9, H^{10}] 3.92, 3.81[s, 12H, OMe]
3b	27.0d, −2.0d, 56.0 [f]	7.0[s, 1H, H^2] 6.08[dd, 1H, H^5, 6.3, 8.8 [d]]	8.24[d, 1H, H_i, 7.3[d]] 1.9[m, 8H, H^9, H^{10}] 3.81, 2.91 [g] [s, 6H, OMe]
4b	63.5d, 51.0d, 10.2 [f]	7.13[s, 1H, H^2] 6.36[dd, 1H, H^5, 6.3, 8.7 [d]]	8.32[d, 1H, H_i, 6.8 [d]] 4.30[m, 1H, H^8] 3.77, 2.12 [g] [s, 6H, OMe] 1.9[m, 8H, H^9, H^{10}]

Table 1 (*Continued*)

Compound	^{31}P	Aromatic	Others
5b	33.2s	6.90[s, 1H, H^2] 5.86[d, 1H, H^5, 6.3 [d]]	8.03[d, 1H, H_i, 7.8 [d]] 4.2[br, 1H, H^8] 1.9[m, 8H, H^9, H^{10}] 3.78, 2.87 [g] [s, 6H, OMe]
1c		6.71, 6.69, 6.55, 6.53[s, 4H, H^2, H^5]	7.44 7.30[s, 2H, H_i] 4.29[m, 2H, H^8] 1.9[m, 8H, H^9, H^{10}] 3.87, 3.80[s, 12H, OMe]

^{31}P NMR: in $CDCl_3$ unless otherwise stated. Measured at 80.9 MHz (ca. ± 20 °C); chemical shifts (δ) in ppm (± 0.1) to high frequency of 85% H_3PO_4. ^1H NMR: in $CDCl_3$. Measured at 200 MHz (ca. ± 20 °C); chemical shifts (δ) in ppm (± 0.01) to high frequency of $SiMe_4$. Coupling constants in Hz. s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; br, broad.

[a] ^3JHH.

[b] $\delta(CH^{acetate}) = 2.14$, 2.11[s, 6H] (compound **1a**); 2.14, 2.13[s, 6H] (compound **1b**).

[c] ^4JHH.

[d] JPH.

[e] δ [$(CH_2)_2CO$] = 2.5 br, ppm.

[f] JPP.

[g] C4–(OMe).

of **c** was identical to the one recorded for **b**. The cyclometallated acetato-bridged complex **1c** was prepared following an analogous procedure to that used for **1b**. The ^1H NMR spectrum of **1c** showed only two resonances for the HC=N proton at δ 7.44 and 7.30, indicating the presence of only two distinct diastereoisomers in solution (**I** and **III**).

The $^{13}C-\{^1H\}$ spectra of the complexes showed the signals assigned to the C6, C=N, and C1 resonances shifted to higher frequency confirming that metallation had occurred [20]. The signals exhibited the splitting due to the mixture of diastereoisomers (see Section 2). Four signals were observed for the C=N carbon atom due to the three pairs of enantiomers present in solution, as opposed to only two signals for the C=N carbon in the spectrum of complex **1c**.

The mass FAB spectrum of **1a** showed a cluster of peaks, centered at 776 and 717 amu which correspond to $[M]^+$ and $[M-AcO]^+$, respectively. The isotopic pattern is in good agreement with the expected dinuclear structure.

The reaction of **1a** and **1b** with aqueous sodium chloride gave the chloro-bridged complexes [Pd{2-$ClC_6H_3C(H)=NCH_2(C_4H_7O)$}(μ-Cl)]$_2$ (**2a**) and [Pd{3,4-$(MeO)_2C_6H_2C(H)=NCH_2(C_4H_7O)$}(μ-Cl)]$_2$ (**2b**), respectively, which were fully characterized (see Table 1 and Section 2). The IR spectra showed the absence of the ν(COO) bands. The ^1H NMR spectra of **2a** and **2b** showed the HC=N resonance at δ 8.21 and δ 7.75, respectively. The aromatic proton resonances of **2a** were at δ 7.23 (H^3) and δ 6.97 (H^4, H^5), as multiplets, whereas two singlets were observed for the H^2, H^5 resonances at δ 6.80 and 6.89, respectively, for compound **2b**. In the $^{13}C-\{^1H\}$ spectra the C=N, C1 and C6 carbon resonances were shifted to higher frequency as compared to the free ligands. The FAB mass spectra showed the peaks which were assigned to the $[M]^+$ and $[M-Cl]^+$ fragments; a similar fragmentation of cyclometallated chloro-bridged complexes has been reported [33].

Reaction of **2a** with PPh_3 in acetone gave the mononuclear cyclometallated complex [Pd{2-$ClC_6H_3C(H)=NCH_2(C_4H_7O)$}(Cl)($PPh_3$)], **3a**, in a typical bridge-splitting reaction. In the ^1H NMR spectra the HC=N and H^5 resonances showed coupling to the phosphorus nucleus [δ 8.62 ($JPH = 8.3$ Hz) and δ 6.25 ($JPH = 6.4$ Hz), respectively]; in the $^{31}P-\{^1H\}$ spectrum the resonance of the coordinated phosphine was a singlet at δ 43.0; these findings are in agreement with a phosphorus *trans* to nitrogen arrangement [34–37]. The FAB mass spectrum showed peaks centered at 627 and 590 amu for the $[M]^+$ and $[M-Cl]^+$ fragments, respectively.

Treatment of **3a** with silver triflate gave the complex [Pd{2-$ClC_6H_3C(H)=NCH_2(C_4H_7O)$}($PPh_3$)][$CF_3SO_3$] (**4a**) after the removal of the AgCl precipitate formed. The most noteworthy differences in the ^1H NMR spectrum of **4a** as compared to **3a**, were in the THF proton resonances, although overlapping of these resonances made an exact assignment difficult, especially in the

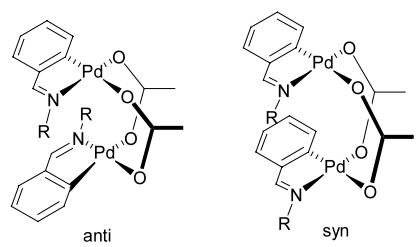


Fig. 1.

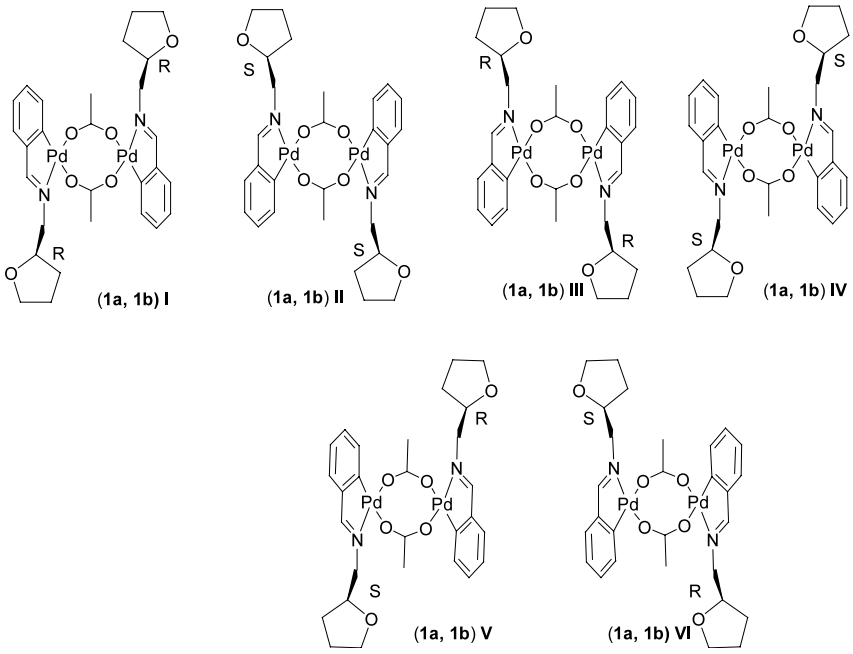


Fig. 2.

splitting pattern shown by the H^7, H^8, and H^{11} protons. Furthermore, the $^{13}C-\{^1H\}$ spectrum of **4a** showed the signal assigned to C8 at δ 81.9, downfield shifted consequent upon Pd–O bond formation (cf. δ 78.6, **a**, and δ 77.5, **3a**). Compound **4a** is a 1:1 electrolyte, as shown by molar conductivity measurements. The FAB-mass spectrum showed a set of peaks centered at 592 amu for the $[M-CF_3SO_3]^+$ fragment.

Pd–O bond formation could also be achieved by reacting **2a** with silver triflate in acetone which gave the complex $[Pd\{2\text{-}ClC_6H_3C(H)=NCH_2(C_4H_7O)\}((CH_3)_2CO)][CF_3SO_3]$ (**5a**) after AgCl removal. The IR spectra supports the presence of the $[CF_3SO_3]^-$ anion, which contains the characteristic stretching bands of the free anion [38], approximately 1274, 1251, 1170 and 1031 cm^{-1}. The ^1H NMR spectrum showed the HC=N resonance at δ 8.07 and the signals corresponding to the H^2, H^3 protons and H^4 as multiplets at δ 6.98 and 6.92, respectively. The splitting pattern and chemical shift resonances for the THF ring are clearly different from those observed in the spectrum of **2a**. In the $^{13}C-\{^1H\}$ spectrum of **4a** the C8 resonance appeared at δ 79.6, downfield shifted upon Pd–O bond formation. Molar conductivity measurements were in agreement with the ionic nature of the complex.

Treatment of complexes **2a** and **2b** with $Ph_2P(CH_2)_3PPh_2$, dppp, in a complex/phosphine 1:1 molar ratio gave the dinuclear cyclometallated complexes $[\{Pd[2\text{-}ClC_6H_3C(H)=NCH_2(C_4H_7O)](Cl)\}_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2)]$ (**8a**) and $[\{Pd[3,4\text{-}(MeO)_2C_6H_2C(H)=NCH_2(C_4H_7O)](Cl)\}_2(\mu\text{-}Ph_2P(CH_2)_3PPh_2)]$ (**5b**) which were fully characterized (see Section 2 and Table 1). The $^{31}P-\{^1H\}$ NMR spectra only showed a singlet resonance in accordance with the centrosymmetric nature of this dinuclear complexes.

In the ^1H NMR spectra of complex **5b**, the C(4)–OCH_3 resonance was shifted towards lower frequency by approximately 0.8 ppm, as compared complex **2b**, due to the shielding effects of the phosphine phenyl ring, in agreement with a N–Pd–P *trans* geometry [16,21,39]. This arrangement was confirmed by the coupling of the HC=N and H^5 proton resonances to the phosphorus nucleus.

Reaction of complexes **2a** and **2b** with the diphosphines $Ph_2P(CH_2)_3Ph_2$, dppp, and $Ph_2PCH=CHPh_2$, *cis*-dppe, in a 1:2 molar ratio gave the mononuclear complexes $[Pd\{2\text{-}ClC_6H_3C(H)=NCH_2(C_4H_7O)\}\{Ph_2P(CH_2)_3Ph_2\text{-}P,P\}][ClO_4]$ (**6a**), $[Pd\{2\text{-}(MeO)_2C_6H_3C(H)=NCH_2(C_4H_7O)\}\{Ph_2P(CH_2)_3Ph_2\text{-}P,P\}][ClO_4]$ (**3b**) and $[Pd\{2\text{-}ClC_6H_3C(H)=NCH_2(C_4H_7O)\}(cis\text{-}Ph_2PCH=CHPh_2\text{-}P,P)][Cl]$ (**4b**) as air-stable solids which were fully characterized (see Table 1 and Section 2).

The $^{31}P-\{^1H\}$ NMR spectra showed two doublets for the two unequivalent phosphorus nuclei. The resonance at lower frequency was assigned to the phosphorus nucleus *trans* to the phenyl carbon atom in accordance with the higher *trans* influence of the latter with respect to the C=N nitrogen atom [40]. The *H*C=N resonance was only coupled to the ^{31}P nucleus *trans* to nitrogen. This was confirmed by selective decoupling experiments on the ^{31}P atoms. The H^5 resonance showed coupling to both phosphorus atoms. Measurements of the specific molar conductivity have shown the complexes to be 1:1 electrolytes.

Reaction of **2a** with the triphosphine bis(2-diphenylphosphinoethyl)phenylphosphine in 1:2 molar ratio, followed by treatment with sodium perchlorate gave [Pd{2-$ClC_6H_3C(H)$=$NCH_2(C_4H_7O)$}{$(PPh_2CH_2CH_2)_2PPh$-*P*,*P*,*P*}][ClO_4] (**7a**). The phosphorus resonances in the $^{31}P-\{^1H\}$ NMR spectrum were downfield shifted from their values in the free phosphine suggesting coordination of the three phosphorus atoms to the metal centre. A triplet resonance at δ 89.3 was assigned to the central ^{31}P nucleus, *trans* to the phenyl carbon atom, and a doublet at δ 45.4 was assigned to the two equivalent mutually *trans* phosphorus nuclei. The latter signal appeared at lower frequency in accordance with the high *trans* influence of the phosphine ligand [11]. The resonance of the proton in the *ortho* position to the metallated carbon appeared as a triplet showing coupling to the central ^{31}P atom [J(PH) 7.8 Hz]; no coupling was observed to the terminal phosphorus nuclei. These data are in accordance with a disposition in which the metallated ring is nearly perpendicular to the plane defined by the three phosphorus atoms; these observations were confirmed by selective decoupling experiments. The shift of the ν(C=N) stretching vibration to lower wavenumbers [27,28] as well as the upfield shift of the HC=N proton resonance in the ^1H NMR spectra [30] indicates the existence of palladium–nitrogen interaction in solution. These results strongly agree with those previously obtained by us in related pentacoordinated palladium(II) species, and hence we propose a similar disposition of the triphos ligand in this case [15]. The C=N signal in the $^{13}C-\{^1H\}$ spectrum at δ 168.8 coupled to the central phosphorus ($JPC = 5.0$ Hz) was also indicative of Pd–N interaction.

Molar conductivity measurements have shown that complex **7a** is a 1:1 electrolyte. The FAB mass spectrum showed a set of peaks centered at 862 amu assigned to the $[M - ClO_4]^+$ fragment.

Acknowledgements

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