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Synthesis and characterization of new oxazoline-based palladacycles with bridging or terminal imidate ligands. Crystal structures of [{Pd(μ-dibromomaleimidate)(Phox)}$_2$], [Pd(dibromomaleimidate)(Phox)(PPh$_3$)] and [Pd(glutarimidate)(Phox)(PPh$_3$)] (Phox = 2-(2-oxazolinyl)phenyl))

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Abstract

The dinuclear hydroxo complex [{Pd(μ-OH)(Phox)}$_2$] (**I**) (Phox = 2-(2-oxazolinyl)phenyl) reacts in a 1:2 molar ratio with several imidate ligands to yield new cyclometallated palladium complexes [{Pd(μ-NCO)(Phox)}$_2$] containing asymmetric imidate –NCO– bridging units. [–NCO– = succinimidate (succ) (**1**), phtalimidate (phtal) (**2**), maleimidate (mal) (**3**), 2,3-dibromomaleimidate (2,3-diBrmal) (**4**) and glutarimidate (glut) (**5**)]. The reaction of these complexes with tertiary phosphines provides novel mononuclear N-bonded imidate derivatives of the general formula [Pd(imidate)(Phox)(PR$_3$)] [R = Ph (**a**), 4-F–C$_6$H$_4$ (**b**) or CH$_2$CH$_2$CN (**c**)]. The new complexes were characterized by partial elemental analyses and spectroscopic methods (IR, FAB, ^{1}H, ^{13}C and ^{31}P). The single-crystal structures of compounds **4**, **4a** and **5a** have been established.

Keywords: Imidate complexes; Cyclometallated palladium(II) complexes; 2-Phenyl-2-oxazoline; X-ray study

1. Introduction

Palladium compounds containing one metal–carbon bond intramolecularly stabilized by a donor heteroatom are one of the most popular classes of organopalladium derivatives. Initial studies dealt with azobenzenes and heteroaromatic ligands that can easily be orthometallated by Pd(II) salts via C(sp^2)–H bond cleavage [1–3] to usually give the corresponding acetate or halide-bridged dimers. These complexes have been employed as convenient precursors of mononuclear and dinuclear cyclometallates [4–12]. Since 1970 to date several reviews have been dedicated to different aspects of their chemistry such as synthesis and structural characterization, their applications in organic synthesis, organometallic catalysis, their use as chiral auxiliaries, mesogenic and luminiscent agents or their presence in medicinal and biological chemistry [13]. Among these fields, it can be said that over the last few years the applicability of palladacycles as precatalyst has been the main focus of attention. In this sense, and stimulated by our recent discovery of imidate effects in Pd-catalysed cross-coupling processes [14], we have reported on the synthesis of dinuclear orthometallated palladium(II) derivatives with

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–NCO– bridging ligands and their use as precursors of mononuclear N-bonded imidate derivatives [15,16]. Those dinuclear and mononuclear derivatives, containing an azobenzene, 2-phenylpyridine or benzoquinoline backbone, have shown to be active catalysts/precatalysts for the Suzuki–Miyaura cross-coupling reactions of aryl bromides with aryl boronic acids, and the Sonogashira reactions of aryl halides (in the presence and absence of Cu(I) salts) [17]. The conversions are dependent, to some extent, on the cyclometallated backbone and the imidate ligand, suggesting a role for these pseudohalides in the catalytic cycle in both cross-coupling processes and encouraging us to expand the range of systems under study.

On the other hand, the synthetic value of palladium(II) and platinum(II) di-μ-hydroxo-complexes is a subject of continuous study [18–22]. During the last few years we have also been developing the usefulness of binuclear hydroxo complexes of palladium, some of them with a cyclometallated backbone [23], in the preparation of an extensive selection of new compounds, by means of a simple acid–base reaction [24].

We report here the use of the hydroxo-complex [{Pd(μ-OH)(Phox)}$_2$] (Phox = 2-(2-oxazolinyl)phenyl) in the preparation of new dinuclear palladium(II) derivatives of simple and sterically not hindered 2-phenyl-2-oxazoline with bridging succinimide, phtalimide, maleimide, 2,3-dibromomaleimide and glutarimide ligands acting in the coordination mode mentioned above. We also describe the synthesis of mononuclear N-bonded imidate derivatives, by the reaction of the corresponding dinuclear precursor with neutral phosphine ligands. X-ray diffraction analyses of both mononuclear (**4a**, **5a**) and binuclear (**4**) derivatives are also given. To date, just three complexes containing an orthopalladated 2-phenyl-2-oxazoline ligand have been crystallographically characterised (searched at the Cambridge Structural Database (CSD) v. 5.28 updated till August 2007) [23a,25].

2. Experimental

2.1. Materials and methods

C, H, and N analyses were carried out with a Carlo Erba instrument. IR spectra were recorded on a Perkin–Elmer spectrophotometer 16F PC FT-IR, using Nujol mulls between polyethylene sheets. NMR data (^{1}H, ^{31}P) were recorded on Bruker Avance 300 spectrometer. Conductance measurements were performed with a Crison 525 conductimeter (in acetone, 5×10^{-4} M). Mass spectrometric analyses were performed on a Fisons VG Autospec double-focusing spectrometer, operated in the negative mode. Ions were produced by fast atom bombardment (FAB) with a beam of 25-keV Cs atoms. The mass spectrometer was operated with an accelerating voltage of 8 kV and a resolution of at least 1000.

The cyclometallated precursors [{Pd(μ-OOCMe)(Phox)}$_2$] [25] and [{Pd(μ-OH)(Phox)}$_2$] [23a] were prepared as described in the literature. The commercially available chemicals were purchased from Aldrich Chemical Co. and were used without further purification, and all the solvents were dried by standard methods before use.

2.2. Synthesis

2.2.1. Preparation of complexes [{Pd(μ-NCO)(Phox)}$_2$] (–NCO– = suc (**1**); R = phtal (**2**); R = mal (**3**); R = 2,3-diBrmal (**4**); R = glut (**5**))

The new complexes were obtained by treating [{Pd(μ-OH)(Phox)}$_2$] with the corresponding imidate ligand in molar ratio 1:2, using $(CH_3)_2CO$ as the solvent and according to the following general method. To an acetone suspension (20 mL) of the precursor (250 mg; 0.464 mmol) was added the stoichiometric amount of the corresponding imidate ligand. The resulting suspension was stirred for 60 min at reflux temperature and then concentrated to a quarter of volume under reduced pressure. Addition of $(CH_3CH_2)_2O$ caused precipitation of the new complexes, which were filtered off, air dried and recrystallised from CH_2Cl_2/C_6H_{14}.

*[{Pd(μ-suc)(Phox)}$_2$] (**1**):* (85% yield). *Anal.* Calc. for $C_{26}H_{24}N_4O_6Pd_2$: C, 44.5; H, 3.5; N, 8.0. Found: C, 44.3; H, 3.6; N, 8.3%. FT-IR (nujol mull cm^{-1}): *ν*(CN–Phox) 1640(vs); *ν*(CO) 1720(vs); 1592(vs). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* ($SiMe_4$) (ppm): 2.17 (m, 4H, suc), 2.79 (m, 6H, 4Hsuc + 2H NCH_2), 3.56 (m, 4H, $2NCH_2 + 2OCH_2$), 4.29 (m, 2H, OCH_2), 6.75 (m, 2H, arom.), 7.04 (m, 6H, arom.). FAB-MS (positive mode) *m/z*: 702 (M^+), 604 (M^+-suc).

*[{Pd(μ-phtal)(Phox)}$_2$] (**2**):* (82% yield). *Anal.* Calc. for $C_{34}H_{24}N_4O_6Pd_2$: C, 51.2; H, 3.0; N, 7.0. Found: C, 51.0; H, 3.3; N, 7.3%. FT-IR (nujol mull cm^{-1}): *ν*(CN–Phox) 1630(vs); *ν*(CO) 1730(vs); 1598(vs). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* ($SiMe_4$) (ppm): 2.90 (m, 2H, NCH_2), 3.58 (m, 4H, $2NCH_2 + 2OCH_2$), 4.33 (m, 2H, OCH_2), 6.84 (m, 2H, phtal), 7.08 (m, 4H, arom.), 7.11 (m, 2H, phtal), 7.53 (m, 4H, arom.), 7.62 (m, 2H, phtal), 7.75 (m, 2H, phtal). FAB-MS (positive mode) *m/z*: 798 (M^+), 652 (M^+-phtal).

*[{Pd(μ-mal)(Phox)}$_2$] (**3**)*: (75% yield). *Anal.* Calc. for $C_{26}H_{20}N_4O_6Pd_2$: C, 44.8; H, 2.9; N, 8.0. Found: C, 45.0; H, 3.0; N, 8.2%. FT-IR (nujol mull cm^{-1}): *ν*(CN–Phox) 1620(vs); *ν*(CO) 1720(vs); 1584(vs). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* ($SiMe_4$) (ppm): 2.86 (m, 2H, NCH_2), 3.58 (m, 4H, $2NCH_2 + 2OCH_2$), 4.34 (m, 2H, OCH_2), 6.65 (d, 2H, mal), 7.00 (m, 4H, 2mal + 2H, arom.), 7.08 (m, 6H, arom.). FAB-MS (positive mode) *m/z*: 698 (M^+), 600 (M^+-mal).

*[{Pd(μ-2,3-diBrmal)(Phox)}$_2$] (**4**)*: (62% yield). *Anal.* Calc. for $C_{26}H_{16}Br_4N_4O_6Pd_2$: C, 30.8; H, 1.6; N, 5.5. Found: C, 30.9; H, 1.7; N, 5.5%. FT-IR (nujol mull cm^{-1}): *ν*(CN-2,3-dibrmal) 1640(vs); *ν*(CO) 1738(s); 1574(s). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* ($SiMe_4$) (ppm): 2.88 (m, 2H, NCH_2), 3.61 (m, 4H, $2NCH_2 + 2OCH_2$), 4.32 (m, 2H, OCH_2), 6.71 (m, 2H, arom.), 7.08 (m, 6H, arom.). FAB-MS (positive mode) *m/z*: 1012 (M^+), 760 (M^+-2,3-diBrmal).

*[{Pd(μ-glut)(Phox)}$_2$] (**5**):* (52% yield). *Anal.* Calc. for $C_{28}H_{28}N_4O_6Pd_2$: C, 44.5; H, 3.5; N, 8.0. Found: C, 44.3; H, 3.6; N, 8.3%. FT-IR (nujol mull cm^{-1}): *ν*(CN–Phox) 1646–1634(vs); *ν*(CO) 1560–1538(vs). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* ($SiMe_4$) (ppm): 1.92 (m, 4H, glut), 2.70–2.44 (m, 10H, 8 glut + 2H NCH_2), 3.52 (m, 4H, $2NCH_2 + 2OCH_2$), 4.27 (m, 2H, OCH_2), 6.66 (m, 2H, arom.), 7.00 (m, 4H, arom.), 7.10 (m, 2H, arom.). FAB-MS (positive mode) *m*/*z*: 729 (M^+), 618 (M^+-glut).

2.2.2. Preparation of complexes

*[Pd(imidate)(Phox)(PR$_3$)] (imidate = suc (**1**); phtal (**2**); mal (**3**); 2,3-diBrmal (**4**); glut (**5**); R = Ph (**a**); 4-F–C_6H_4 (**b**); CH_2CH_2CN(**c**))*

The new complexes were obtained by treating the former bridging imidate complexes [{Pd(μ–NCO–)(Phox)}$_2$] with the corresponding phosphine in molar ratio 1:2, using CH_2Cl_2 as the solvent and according to the following general method. To a CH_2Cl_2 suspension (20 mL) of the precursor (0.142 mmol) was added the stoichiometric amount of the corresponding phosphine ligand. The resulting suspension was stirred for 90 min at reflux temperature and then concentrated to a quarter of the volume under reduced pressure. Addition of C_6H_{14} caused the precipitation of the new complexes, which were filtered off, air-dried and recrystallised from CH_2Cl_2/C_6H_{14}.

*[Pd(suc)(Phox)(PPh$_3$)] (**1a**):* (84% yield). *Anal.* Calc. for $C_{31}H_{27}N_2O_3PPd$: C, 60.7; H,4.4; N, 4.6. Found: C, 60.8; H, 4.5; N, 4.6%. FT-IR (nujol mull cm^{-1}): *ν*(CN–Phox) 1625(vs); *ν*(CO) 1618(vs); *ν*(PPh_3) 534(m). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* ($SiMe_4$) (ppm): 1.7–1.87 (m, 2H, suc), 2.2–2.3 (m, 2H, suc), 3.97 (m, 2H, NCH_2), 4.75 (m, 2H, OCH_2), 6.51 (1H, arom.), 6.60 (1H, arom.), 6.96 (1H, arom.), 7.43 (m, 10H, 9PPh_3 + 1H arom.), 7.82 (m, 6H, PPh_3). ^{31}P NMR (300 MHz, $CDCl_3$): *δ* (ppm): 41.9 (s). FAB-MS (positive mode) *m*/*z*: 514 (M^+-suc).

*[Pd(suc)(Phox){P(4-F–C_6H_4)$_3$}] (**1b**):* (77% yield). *Anal.* Calc. for $C_{31}H_{24}F_3N_2O_3PPd$: C, 55.8; H, 3.6; N, 4.2. Found: C, 55.9; H, 3.7; N, 4.2%. FT-IR (nujol mull cm^{-1}): *ν*(CN–Phox) 1642(vs); *ν*(CO) 1620(vs); *ν*(P(C_6H_4F)$_3$) 536(m). ^{1}H NMR (300 MHz, $CDCl_3$): d ($SiMe_4$) (ppm): 1.83 (m, 2H, suc), 2.29 (m, 2H, suc), 3.94 (m, 2H, NCH_2), 4.72 (m, 2H, OCH_2), 6.41 (1H, arom.), 6.70 (1H, arom.), 6.92 (1H, arom.), 7.08 (m, 6H, phosphine), 7.30 (1H, arom.), 7.76 (m, 6H, phosphine). ^{31}P NMR (300 MHz, $CDCl_3$): *δ* (ppm): 39.6 (s). FAB-MS (positive mode) *m*/*z*: 568 (M^+-suc).

*[Pd(suc)(Phox){P(CH_2CH_2CN)$_3$}] (**1c**):* (76% yield). *Anal.* Calc. for $C_{22}H_{24}N_5O_3PPd$: C, 48.6; H,4.5; N, 12.9. Found: C, 48.7; H, 4.5; N, 12.9%. FT-IR (nujol mull cm^{-1}): *ν*(CN–Phox) 1625(vs); *ν*(CO) 1614(vs); *ν*(C≡N) 2240(s). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* ($SiMe_4$) (ppm): 1.99 (m, 2H, suc), 2.39 (m, 6H, phosphine), 2.75 (m, 8H, 6H phosphine + 2H suc), 3.84 (m, 2H, NCH_2), 4.71 (m, 2H, OCH_2), 6.95–7.41 (m, 4H, arom.). ^{31}P NMR (300 MHz, $CDCl_3$): *δ* (ppm): 32.3 (s). FAB-MS (positive mode) *m*/*z*: 442 (M^+-suc).

*[Pd(phtal)(Phox)(PPh$_3$)] (**2a**):* (72% yield). *Anal.* Calc. for $C_{35}H_{27}N_2O_3PPd$: C, 63.6; H, 4.1; N, 4.2. Found: C, 63.8; H, 4.2; N, 4.2%. FT-IR (nujol mull cm^{-1}): *ν*(CN–Phox) 1622(vs); *ν*(CO) 1644(vs); *ν*(PPh_3) 534(m). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* ($SiMe_4$) (ppm): 3.92 (m, 2H, NCH_2); 4.66 (m, 2H, OCH_2); 6.55 (1H, arom.), 6.68 (1H, arom.), 6.98 (1H, arom.), 7.43 (m, 14H, 4H phtal + 9H PPh_3 + 1H arom.); 7.76 (m, 6H, PPh_3). ^{31}P NMR (300 MHz, $CDCl_3$): *δ* (ppm): 41.9(s). FAB-MS (positive mode) *m*/*z*: 514 (M^+-phtal).

*[Pd(phtal)(Phox){P(4-F–C_6H_4)$_3$}] (**2b**):* (84% yield). *Anal.* Calc. for $C_{35}H_{24}F_3N_2O_3PPd$: C, 58.8; H, 3.4; N, 3.9. Found: C, 58.9; H, 3.6; N, 3.9%. FT-IR (nujol mull cm^{-1}): *ν*(CN–Phox) 1620(vs); *ν*(CO) 1644(vs); *ν*(P(C_6H_4F)$_3$) 536(m). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* ($SiMe_4$) (ppm): 3.93 (m, 2H, NCH_2); 4.69 (m, 2H, OCH_2); 6.44 (1H, arom.); 6.71 (1H, arom.); 6.92–6.97 (m, 7H, 1H, arom. + 6H phosphine); 7.26 (1H, arom., Phox); 7.37 (s, 4H, phtal); 7.72 (m, 6H, phosphine). ^{31}P NMR (300 MHz, $CDCl_3$): *δ* (ppm): 39.8(s). FAB-MS (positive mode) *m*/*z*: 715 (M^+); 568 (M^+-phtal).

*[Pd(phtal)(Phox){P(CH_2CH_2CN)$_3$}] (**2c**):* (78% yield). *Anal.* Calc. for $C_{26}H_{24}N_5O_3PPd$: C, 52.8; H, 4.1; N, 11.8. Found: C, 52.9; H, 4.2; N, 11.9%. FT-IR (nujol mull cm^{-1}): *ν*(CN–Phox) 1620(vs); *ν*(CO) 1650(vs); *ν*(C≡N) 2242(s). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* ($SiMe_4$) (ppm): 2.45 (m, 6H, phosphine), 2.89 (m, 6H, phosphine), 3.72 (m, 2H, NCH_2), 4.64 (m, 2H, OCH_2), 6.97–7.42 (m, 4H, arom.); 7.49–7.69 (m, 4H, phtal). ^{31}P NMR (300 MHz, $CDCl_3$): *δ* (ppm): 32.4 (s). FAB-MS (positive mode) *m*/*z*: 591 (M^+); 444 (M^+-phtal).

*[Pd(mal)(Phox)(PPh$_3$)] (**3a**):* (64% yield). *Anal.* Calc. for $C_{31}H_{25}N_2O_3PPd$: C, 60.9; H, 4.1; N, 4.6. Found:C, 70.0; H, 4.2; N, 4.6%. FT-IR (nujol mull cm^{-1}): *ν*(CN–Phox) 1620(vs); *ν*(CO) 1634(vs); *ν*(PPh_3) 534(m). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* ($SiMe_4$) (ppm): 3.89 (m, 2H, NCH_2); 4.68 (m, 2H, OCH_2); 6.05 (s, 2H, mal); 6.49 (m, 1H, arom.); 6.64 (m, 1H, arom.); 6.89 (m, 1H, arom.); 7.25 (m, 1H, arom.); 7.34 (m, 9H, PPh_3); 7.74 (m, 6H, PPh_3). ^{31}P NMR (300 MHz, $CDCl_3$): *δ* (ppm): 41.8 (s). FAB-MS (positive mode) *m*/*z*: 514 (M^+-mal).

*[Pd(mal)(Phox){P(4-F–C_6H_4)$_3$}] (**3b**):* (68% yield). *Anal.* Calc. for $C_{31}H_{22}F_3N_2O_3PPd$: C, 56.0; H, 3.3; N, 4.2. Found: C, 56.1; H, 3.5, N, 4.2%. FT-IR (nujol mull cm^{-1}): *ν*(CN–Phox) 1600(vs); *ν*(CO) 1642(vs); *ν*(P(C_6H_4F)$_3$) 536(m). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* ($SiMe_4$) (ppm): 3.88 (m, 2H, NCH_2); 4.70 (m, 2H, OCH_2); 6.12 (s, 2H, mal); 6.41 (1H, arom.); 6.69 (1H, arom.); 6.94 (1H, arom.); 7.04 (m, 6H, phosphine); 7.29 (1H, arom.); 7.70 (m, 6H, phosphine). ^{31}P NMR (300 MHz, $CDCl_3$): *δ* (ppm): 39.6(s). FAB-MS (positive mode) *m*/*z*: 568 (M^+-mal).

*[Pd(mal)(Phox){P(CH_2CH_2CN)$_3$}] (**3c**):* (69% yield). *Anal.* Calc. for $C_{22}H_{22}N_5O_3PPd$: C, 48.8; H, 4.1; N, 12.9. Found: C, 48.9; H, 4.2; N, 13.0%. FT-IR (nujol mull cm^{-1}): *ν*(CN–Phox) 1620(vs); *ν*(CO) 1644(vs); *ν*(C≡N) 2242(s). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* ($SiMe_4$)

(ppm): 2.40 (m, 6H, phosphine); 2.83 (m, 6H, phosphine); 3.78 (m, 2H, NCH_2); 4.69 (m, 2H, OCH_2); 6.60 (s, 2H, mal); 6.70 (m, 1H, arom.); 7.0 (m, 1H, arom.); 7.18 (m, 1H, arom.); 7.39 (m, 1H, arom.). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm): 32.3(s). FAB-MS (positive mode) *m/z*: 444 (M^+-mal).

[Pd(2,3-diBrmal)(Phox)(PPh$_3$)] (**4a**): (68% yield). *Anal.* Calc. for $C_{31}H_{23}Br_2N_2O_3PPd$: C, 48.4; H, 3.0; N, 3.6. Found: C, 48.5; H, 3.1; N, 3.6%. FT-IR (nujol mull cm^{-1}): ν(CN–Phox) 1640(vs); ν(CO) 1654(vs); ν(PPh_3) 534(m). ^1H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$) (ppm): 3.92 (m, 2H, NCH_2); 4.66 (m, 2H, OCH_2); 6.40 (m, 1H, arom.); 6.65 (m, 1H, arom.); 6.92 (m, 1H, arom.); 7.25–7.50 (m, 10H, 9PPh_3 + 1H arom.); 7.76 (m, 6H, PPh_3). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm): 41.9(s). FAB-MS (positive mode) *m/z*: 768 (M^+), 514 (M^+-2,3-diBrmal).

[Pd(2,3-diBrmal)(Phox){P(4-F–C$_6$H$_4$)$_3$}] (**4b**): (82% yield). *Anal.* Calc. for $C_{31}H_{20}Br_2F_3N_2O_3PPd$: C, 45.3; H, 2.5; N, 3.4. Found: C, 45.4; H, 2.5, N, 3.4%. FT-IR (nujol mull cm^{-1}): ν(CN–Phox) 1642(vs); ν(CO) 1658(vs); ν(P(*p*-$C_6H_4F)_3$) 540(m). ^1H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$) (ppm): 3.91 (m, 2H, NCH_2); 4.71 (m, 2H, OCH_2); 6.37 (m, 1H, arom.); 6.69 (m, 1H, arom.); 7.06 (m, 7H, 6H phosphine + 1H, arom. Phox); 7.29 (1H, arom.); 7.69 (m, 6H, phosphine). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm): 39.6(s). FAB-MS (positive mode) *m/z*: 822 (M^+), 568 (M^+-2,3-diBrmal).

[Pd(2,3-diBrmal)(Phox){P(CH$_2$CH$_2$CN)$_3$}] (**4c**): (72% yield). *Anal.* Calc. for $C_{22}H_{20}Br_2N_5O_3PPd$: C, 37.8; H, 2.9; N, 10.0. Found: C, 37.9; H, 3.0; N, 10.1%. FT-IR (nujol mull cm^{-1}): ν(CN–Phox) 1642(vs); ν(CO) 1656(vs); ν(C≡N) 2244(s). ^1H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$) (ppm): 2.27 (m, 6H, phosphine); 2.83 (m, 6H, phosphine); 3.95 (m, 2H, NCH_2); 4.63 (m, 2H, OCH_2); 7.18–7.31 (m, 2H, arom.), 7.40–7.52 (m, 2H, arom.). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm): 42.06(s). FAB-MS (positive mode) *m/z*: 445 (M^+-2,3-diBrmal).

[Pd(glut)(Phox)(PPh$_3$)] (**5a**): (53% yield). *Anal.* Calc. for $C_{32}H_{29}N_2O_3PPd$: C, 61.3; H, 4.7; N, 4.5. Found: C, 61.6; H, 4.8; N, 4.7%. FT-IR (nujol mull cm^{-1}): ν(CN–Phox) 1644(vs); ν(CO) 1574(vs); ν(PPh_3) 534(m). ^1H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$) (ppm): 1.24 (m, 2H, glut); 1.63 (m, 2H, glut); 2.16 (m, 2H, glut); 3.86 (m, 2H, NCH_2); 4.68 (m, 2H, OCH_2); 6.47 (m, 1H, arom.); 6.62 (m, 1H, arom.); 6.86 (m, 1H, arom.); 7.23 (m, 1H, arom.); 7.36 (m, 9H, phosphine); 7.82 (m, 6H, phosphine). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm): 42.4(s). FAB-MS (positive mode) *m/z*: 626 (M^+), 514 (M^+-glut).

[Pd(glut)(Phox){P(4-F–C$_6$H$_4$)$_3$}] (**5b**): (60% yield). *Anal.* Calc. for $C_{32}H_{26}F_3N_2O_3PPd$: C, 56.4; H, 3.9; N, 4.1. Found: C, 56.5; H, 4.0; N, 4.3%. FT-IR (nujol mull cm^{-1}): ν(CN–Phox) 1644(vs); ν(CO) 1588(vs); ν(P(*p*-$C_6H_4F)_3$) 536(m). ^1H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$) (ppm): 1.32 (m, 2H, glut); 1.57 (m, 2H, glut); 2.21 (m, 2H, glut); 3.84 (m, 2H, NCH_2); 4.69 (m, 2H, OCH_2); 6.36 (m, 1H, arom.); 6.65 (m, 1H, arom.); 6.90 (m, 1H, arom.); 7.05 (m, 6H, phosphine); 7.28 (m, 1H, arom.); 7.05 (m, 6H, phosphine). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm): 40.3(s). FAB-MS (positive mode) *m/z*: 679 (M^+), 568 (M^+-glut).

[Pd(glut)(Phox){P(CH$_2$CH$_2$CN)$_3$}] (**5c**): (49% yield). *Anal.* Calc. for $C_{23}H_{26}N_5O_3PPd$: C, 49.5; H, 4.7; N, 8.6. Found: C, 49.7; H, 4.6; N, 8.7%. FT-IR (nujol mull cm^{-1}): ν(CN–Phox) 1646(vs); ν(CO) 1578(vs); ν(C≡N) 2245(s). ^1H NMR (300 MHz, $CDCl_3$): δ ($SiMe_4$) (ppm): 1.95 (m, 2H glut); 2.26–2.40 (m, 6H, phosphine) 2.48–2.61 (m, 4H, glut); 2.75–2.93 (m, 6H, phosphine); 3.76 (m, 2H, NCH_2); 4.70 (m, 2H, OCH_2); 7.00 (m, 1H, arom.); 7.10–7.25 (m, 2H, arom); 7.38 (m, 1H, arom). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm): 31.4(s). FAB-MS (positive mode) *m/z*: 445.1 (M^+-glut).

2.3. Crystal structure determination of [{Pd(μ-2,3-diBrmal)(Phox)}$_2$] (4), [Pd(2,3-diBrmal)(Phox)(PPh$_3$)] (4a) and [Pd(glut)(Phox)(PPh$_3$)] (5a)

Crystals suitable for a diffraction study were prepared by a slow diffusion of hexane into their CH_2Cl_2 solutions. Crystallographic data are summarized in Table 1. Data collection for **4** and **4a** was performed at −173 °C on a Bruker Smart CCD diffractometer with a nominal crystal to detector distance of 4.5 cm. Diffraction data were collected based on a ω scan run. A total of 2524 frames were collected at 0.3° intervals and 10 s per frame. The diffraction frames were integrated using the SAINT package [26] and corrected for absorption with SADABS [27]. For **5a** data collection was performed at 293 K on a Nonius Kappa-CCD single crystal diffractometer. Crystal-detector distance was fixed at 35 mm, and a total of 122 images were collected using the oscillation method, with scan angle per frame, 2° oscillation and 20 s exposure time per image. Data collection strategy was calculated with the program COLLECT [28]. Data reduction and cell refinement were performed with the programs HKL DENZO and SCALEPACK [29].

The structures were solved by direct methods [30] and refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-H atoms [30] (Table 1). Hydrogen atoms were introduced in the calculated positions and refined during the last stages of the refinement.

3. Results and discussion

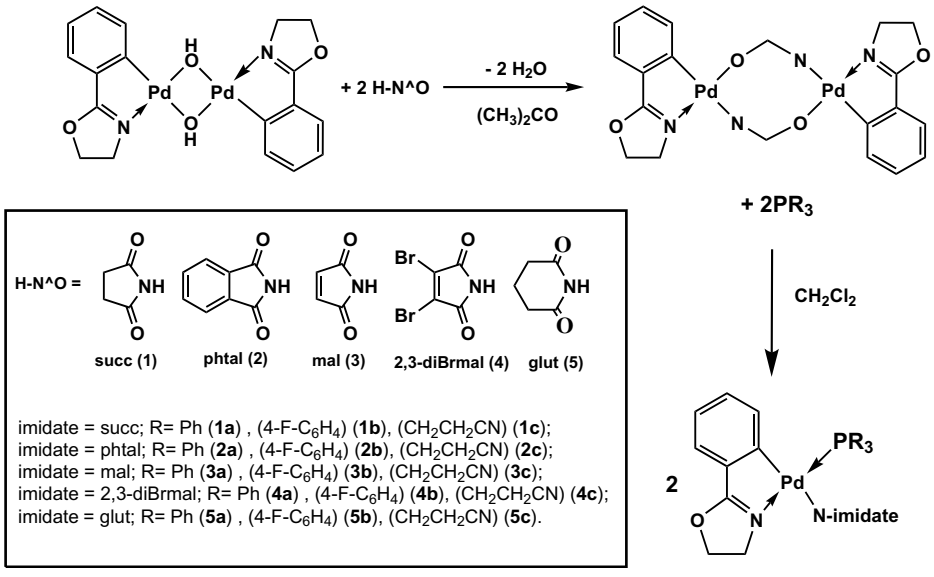
Under the conditions described in Section 2, [{Pd(μ-OH)(Phox)}$_2$] reacts with several imidate-type ligands to give dinuclear complexes **1**–**5** in which the imidate ligands replace the bridging hydroxo group as presented in Scheme 1.

Both the precursor and the new complexes are quite insoluble in the reaction media, so that just a change in the suspension colour is observed. The new 2-(2-oxazolinyl)phenyl) derivatives are air-stable yellow solids and their infrared spectra show only one absorption around 730 cm^{-1}, as expected for the region of out-of-plane C–H bending in disubstituted arenes. Also the characteristic

Table 1
Crystal data and structure refinement for compounds **4**, **4a** and **5a**

	4 · CH_2Cl_2	**4a**	**5a** · $1/2CH_2Cl_2$
Empirical formula	$C_{27}H_{18}Br_4Cl_2N_4O_6Pd_2$	$C_{31}H_{23}Br_2N_2O_3PPd$	$C_{32.5}H_{30}ClN_2O_3PPd$
Formula weight	1097.79	768.70	653.90
Temperature (K)	100(2)	100(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P*21/*n*	*C*2/*c*	*C*2/*c*
Unit cell dimensions			
a (Å)	8.5336(3)	23.3725(11)	26.6920(5)
b (Å)	22.9656(9)	11.7735(6)	16.6670(4)
c (Å)	16.5248(7)	20.2239(10)	15.8240(3)
β (°)	102.0920(10)	95.2240(10)	119.8430(10)
V (Å^3)	3166.7(2)	5542.0(5)	6106.2(2)
Z	4	8	8
D_{calc} (Mg m^{-3})	2.303	1.843	1.423
Absorption coefficient (mm^{-1})	6.401	3.649	0.702
F(000)	2088	3024	2648
Crystal size (mm^3)	0.08 × 0.07 × 0.04	0.27 × 0.25 × 0.15	0.60 × 0.02 × 0.02
θ Range for data collection (°)	1.54–28.19	1.75–28.18	1.51–27.52
Index ranges	$-11 \leqslant h \leqslant 11$	$-30 \leqslant h \leqslant 30$	$-34 \leqslant h \leqslant 34$
	$-29 \leqslant k \leqslant 29$	$-15 \leqslant k \leqslant 15$	$-19 \leqslant k \leqslant 21$
	$-20 \leqslant l \leqslant 20$	$-26 \leqslant l \leqslant 26$	$-20 \leqslant l \leqslant 20$
Reflections collected	36697	31927	12355
Independent reflections [R_{int}]	7367 [0.0394]	6468 [0.0353]	6994 [0.0554]
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/parameters	7367/425	6468/361	6994/362
R^a, Rw^b [$I > 2\sigma(I)$]	$R_1 = 0.0315$, $wR_2 = 0.0696$	$R_1 = 0.0375$, $wR_2 = 0.0793$	$R_1 = 0.1056$, $wR_2 = 0.3249$
R^a, Rw^b [all data]	$R_1 = 0.0430$, $wR_2 = 0.0816$	$R_1 = 0.0397$, $wR_2 = 0.0804$	$R_1 = 0.1575$, $wR_2 = 0.3495$
S^c	0.794	1.202	2.103
Maximum, minimum $\Delta\rho$ (e Å^{-3})	2.518, −2.082	0.953, −0.386	2.691, −5.682

[a] $R = \sum \|F_o| - |F_C\| / \sum |F_o|$.
[b] $Rw = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/\sigma^2(|F_o^2|)$.
[c] $S = [\sum[w(F_o^2 - F_c^2)^2] / (N_{obs} - N_{param})]^{1/2}$.



Scheme 1.

C=N absorption of the cyclometallated ligand around 1630 cm^{-1} is observed, shifted to lower frequencies compared to the free ligand (1649 cm^{-1}) and partially overlapped with those two strong bands attributed to imidato-carbonyl stretching in the range 1738–1720 and 1598–1562 cm^{-1}, respectively. According to the previously reported data [10] the appearance of two bands in this region suggests the coordination of one carbonyl group

to the metal as a part of an –NCO– bridging unit. Support for the proposed dinuclearity of complexes **1**–**5** comes from the FAB mass spectrometry, as can be implied by the *m*/*z* values for the observed fragments. Spectra of the new bridged compounds show a similar fragmentation pattern which includes the peaks corresponding to $[M]^+$, $[M^+$-imidate$]^+$ and $[Pd(Phox)]^+$. The abundances of the signals around the pattern ion are consistent with the natural isotopic ones.

Despite the low solubility in common solvents of some of the new derivatives, further evidence of the proposed coordination comes from the ^{1}H NMR spectroscopy. It has been reported for the related complex $[\{Pd(\mu\text{-OOCMe})(Phox)\}_2]$ that, as a consequence of its open-book structure, each of the two methylene protons of the oxazoline ring is non-equivalent, displaying a set of three unresolved multiplets (ratio 1:2:1) [25]. In $CDCl_3$ the new binuclear complexes showed this behaviour for the oxazoline protons, which appeared in the spectra together with the expected resonances of the imidate ligands (see Section 2). The preparation of single crystals of complex **4** suitable for X-ray diffraction was also possible and unambiguously confirmed the molecular structure. This is presented in Fig. 1 together with selected bond distances and angles.

The unit cell of complex **4** contains two molecules. In accordance with the geometries displayed by the previously

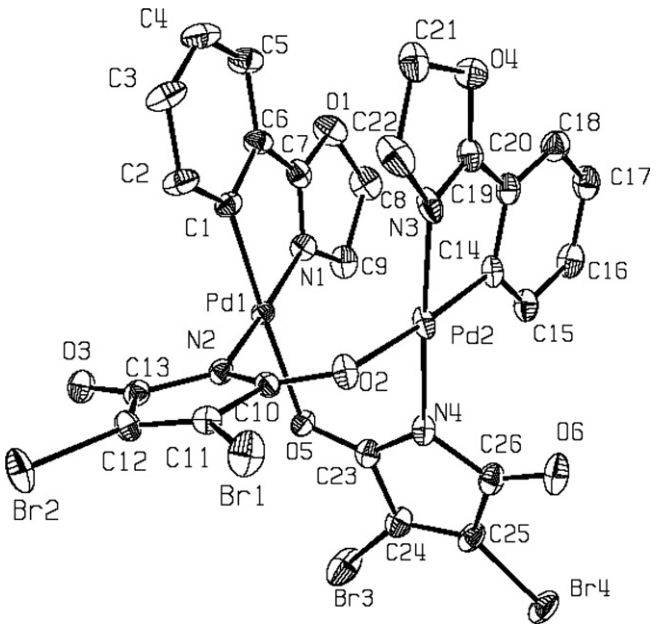


Fig. 1. ORTEP diagram of complex **4** with the atom numbering scheme; thermal ellipsoids are drawn at the 50% propability level. Hydrogen atoms are omitted for clarity. Selected distances (Å): Pd(1)–C(1) 1.976(4); Pd(1)–N(1) 2.017(3); Pd(1)–N(2) 2.024(3); Pd(1)–O(5) 2.175(3); Pd(1)–Pd(2) 2.9279(4); Pd(2)–C(14) 1.980(4); Pd(2)–N(3) 2.024(4); Pd(2)–N(4) 2.030(4); Pd(2)–O(2) 2.189(3). Selected angles (°): C(1)–Pd(1)–N(1) 81.08(6); C(1)–Pd(1)–N(2) 92.68(15); N(1)–Pd(1)–N(2) 172.91(14); C(1)–Pd(1)–O(5) 175.64(14); N(1)–Pd(1)–O(5) 94.56(13); N(2)–Pd(1)–O(5) 91.66(12); C(14)–Pd(2)–N(3) 81.42(16); C(14)–Pd(2)–N(4) 92.53(16); N(3)–Pd(2)–N(4) 173.82(14); C(14)–Pd(2)–O(2) 173.71(15); N(3)–Pd(2)–O(2) 92.47(13); N(4)–Pd(2)–O(2) 93.61(13).

reported oxazoline-derived μ-chloro [31] and μ-acetate dimers [32], an *anti*-arrangement of identical donor atoms is found, supporting the pseudohalide character of imidate ligands. Also in common with the mentioned compounds and our previously described structure $[\{Pd(\mu\text{-suc})(Phpy)\}_2]$ [15] is the so-called open-book geometry accompanied by a rather short Pd(1)–Pd(2) distance of 2.9279(4) Å, within the generally accepted value for a Pd–Pd intramolecular interaction (<3.00 Å). An interesting structural aspect is that two hydrogens bonded to C22 ad C8, respectively, point towards the centre of the phenyl rings: distance H22B-centroid (C1–C6) = 3.106 Å; distance H8A-centroid (C14–C19) = 3.199 Å, suggesting an interaction between the rings of the two cyclometallated ligands. We have recently developed methods for the conformational classification of eight-membered rings [33]. From this perspective the Pd1–N2–C10–O2–Pd2–N4–C23–O5 ring displays a chair-chair conformation (CC = 0.9985; TCC = 0.0015 for $\sigma = 10$). Using the same Classification method, the five-membered palladacycles Pd1–C1–C6–C7–N1 and Pd2–C14–C19–C20–N3 exhibit almost planar conformations for $\sigma = 10$ (HC = 0.5095; E = 0.4905 and HC = 0.5138; E = 0.4862, respectively).

The structure around the two palladium atoms may be described as nearly planar, and their deviation from the planar coordination has been quantified by measures of improper torsion angles: 2.38° and −0.00° for Pd1 (square pyramidal); −0.96° and −1.01° for Pd2 (tetrahedral) [16]. In the 2,3-dibromomaleimide ligand the C=O distance, 1.228(5) and 1.232(5) Å, is elongated in the bridged group with respect to the non-coordinated C=O, 1.208(5) Å, in both Pd atoms.

As expected, the reactions of the imidate-bridged compounds against tertiary phosphines take place *via* bridge-splitting to yield the mononuclear N-bonded imidate derivatives $[Pd(imidate)(Phox)(PR_3)]$ presented in Scheme 1.

The yellow to orange air-stable solids display negligible molar conductivity values, and their IR spectra show the expected bands for the 2-(2-oxazolinyl)phenyl backbone, together with those attributed to the incoming phosphine ligand and just one strong carbonyl band around 1630 cm^{-1}, typical of N-bonded imidate ligands. The characterisation in solid state was completed with the FAB mass spectrometry, that shows fragments at $[M^+$-imidate] in all cases, being also possible to detect $[M^+]$ and $[Pd(Phox)]^+$ for several compounds. The ^{1}H and ^{31}P NMR data of the mononuclear complexes are collected in Section 2, the latter consisting of singlets with chemical shifts in the usual range of Pd(II) complexes. With regard to the ^{1}H NMR spectra, they show the expected resonances of the cyclometallated 2-phenyl-2-oxazoline, now with just two triplets for the NCH_2 and OCH_2 protons in the 3.70–4.80 ppm region, together with those signals attributed to the corresponding imidate ligand and coordinated phosphine.

The structures of $[Pd(2,3\text{-diBrmal})(Phox)(PPh_3)]$ (**4a**) and $[Pd(glut)(Phox)(PPh_3)]$ (**5a**) have been confirmed by X-ray diffraction study and are presented together with

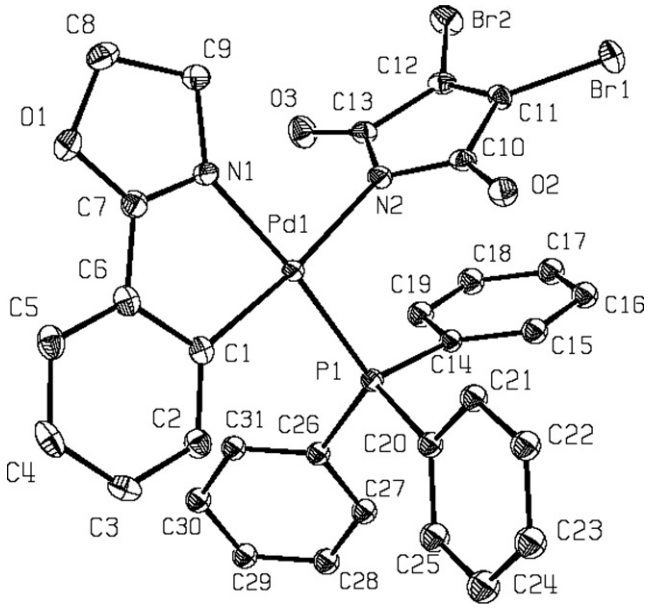


Fig. 2. ORTEP diagram of complex **4a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å): Pd(1)–C(1) 2.027(3); Pd(1)–N(1) 2.068(3); Pd(1)–N(2) 2.113(3); Pd(1)–P(1) 2.2438(9). Selected angles (°): C(1)–Pd(1)–N(1) 81.04(12); C(1)–Pd(1)–N(2) 171.23(12); N(1)–Pd(1)–N(2) 91.43(11); C(1)–Pd(1)–P(1) 94.19(10); N(1)–Pd(1)–P(1) 174.12(8); N(2)–Pd(1)–P(1) 93.58(8).

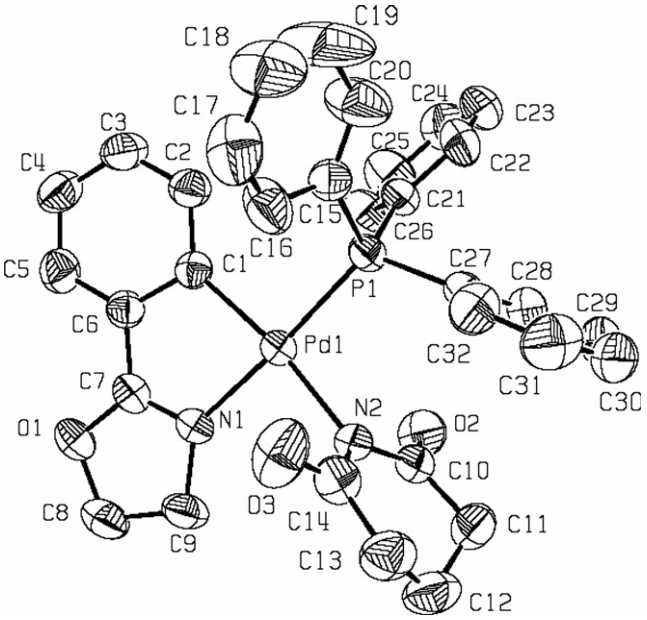


Fig. 3. ORTEP diagram of complex **5a**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å): Pd(1)–C(1) 2.046(12); Pd(1)–N(1) 2.062(10); Pd(1)–N(2) 2.091(10); Pd(1)–P(1) 2.246(3). Selected angles (°): C(1)–Pd(1)–N(1) 81.0(4); C(1)–Pd(1)–N(2) 171.4(4); N(1)–Pd(1)–N(2) 91.4(4); C(1)–Pd(1)–P(1) 94.8(4); N(1)–Pd(1)–P(1) 175.5(3); N(2)–Pd(1)–P(1) 92.9(3).

the selected bond distances and angles in Figs. 2 and 3, respectively. The coordination around the Pd atoms based on measures of torsion angles is approximately planar with slight tetrahedral distortion [16] (N1–C1–P1–Pd1 is 2.67° and −1.14°; N2–P1–C1–Pd1 2.72° and −2.42°, respectively). The displacement of the Pd atom from the mean coordination plane is 0.0524(57) and 0.1586(92) Å (rms = 0.0139 and 0.0017, respectively).

The N–Pd–C angle in the orthometallated moiety, around 81.0° in the three complexes, is similar to that found in complexes containing the same ligand [25,31,32]. The structural analysis of complexes **4a** and **5a** confirms the relative *cis*-position of the phosphine ligand and the metallated carbon atom suggested by the NMR data. This is the typical arrangement of the phosphine group in cyclopalladated complexes of the type [Pd(C^N)(phosphine)(X)] (X = anionic monodentate ligand) due to the so-called *transphobia* effect [34,35]. Following the classification of Dance and Scudder [36] for PPh_3 based on measures of torsion angles M–P–C_{ipso}–C, the conformation of Pd–PPh_3 groups is described as *no rotor* for the new complexes, presenting values $T_3 - T_2 = 38.55°$; $T_2 - T_1 = 31.28°$ for **4a** and $T_3 - T_2 = 22.17°$; $T_2 - T_1 = 88.30°$ for **5a**, that differ to those which would have the ideal *rotor* ($T_1 = T_2 = T_3 = 44°$).

As found for complexes **4**, **4a** and **5a** also display almost planar conformations in the five-membered palladacycles Pd1–C1–C6–C7–N1 (HC = 0.5138; E = 0.4862 and HC = 0.5114; E = 0.4886).

In complex **4a**, the C10–O2 and C13–O3 distances of 2,3-dibromomaleimide ligand are 1.204(4) and 1.209(4) Å, very close to the non-coordinated C=O distances in dinuclear complex **4** (1.208(5) Å). In complex **5a** those distances are slightly higher: 1.216(16) and 1.227(16) Å.

4. Conclusions

Twenty new imidate-palladium(II) complexes with 2-phenyl-2-oxazoline acting as cyclometallated backbone have been prepared and characterized by spectroscopic techniques and single crystal X-ray diffraction analysis. Imidate ligands exhibit two different coordination modes: –NCO– bridging two Pd atoms or N-bonded. We enlarge in this paper the range of imidate and phosphine systems under study in comparison with our previous results, and we present the first X-ray crystal structures of complexes containing 2,3 dibromomaleimide (bonded as –NCO– bridging group (**4**) and as N-bonded (**4a**)), as searched at the Cambridge Structural Database (CSD) v. 5.28 updated till August 2007. Preliminary results show that the new complexes are active catalysts/precatalysts in Suzuki–Miyaura cross-coupling reactions of aryl bromides with aryl boronic acids. A comprehensive study will be reported in due course.

5. Supplementary data

CCDC 671662, 671663 and 671664 contain the supplementary crystallographic data for **4**, **4a** and **5a**. These data

can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

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