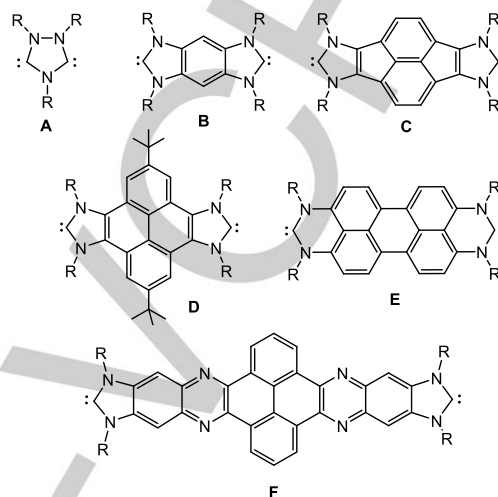# Structural features of mono and dimetallic complexes of palladium combining two types of aromatic NHC ligands

Sergio Gonell,*[a] Eduardo Peris,[b] and Macarena Poyatos*[b]

Abstract: A family of palladium complexes that combine two types of aromatic N-heterocyclic carbene (NHC) ligands has been prepared starting from dinuclear palladium complexes. Two of the complexes are mono-metallic and contain a pyrene-based mono-NHC and a benzimidazolylidene ligand. The other two are dimetallic and combine a bridging pyrene-based bis-NHC ligand with benzimidazolylidene ligands. All new complexes therefore contain two types of NHC ligands that differ in the size of their aromatic backbones coordinated to the same metal center. All complexes have been characterized and the molecular structure of two of them has been confirmed by X-Ray diffraction studies.

Scheme 1. Selected *Janus* type bis-NHC ligands with different polyaromatic cores

Introduction

Poly-metallic compounds represent an interesting type of complexes that have been object of intense research during the last years. The fact that different metal centers are bridged through a common ligand, and therefore located in a close proximity, can provide synergetic effects and unique properties, which are often not accessible by combining the mono-metallic analogs.[1-2] When designing this type of compounds, one crucial parameter to consider is the type of ligand used to bridge/connect the different metal centers. In this regard, properties as flexibility, electronic communication and donor ability of the bridging ligands need to be finely tuned in order to enhance the benefits of the multimetallic compounds.[3] Although a number of ligands have been used in order to achieve this goal, N-heterocyclic carbenes (NHCs)[4-5] are located in a privileged position because their synthetic versatility and good donating ability usually yield complexes with higher stability and improved catalytic properties.[2, 6-7] Furthermore, the rigid nature of some poly-NHCs allows stablishing fixed distances between the metal centers connected by these polydentate ligands.[8-9] In particular, facially opposed bis-NHCs (*Janus*-type bis-carbenes, Scheme 1) have been widely used to construct bimetallic complexes[10-11] and organometallic polymers.[10, 12]

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One general strategy for synthesizing geometrically isolated bis-NHCs is the direct annulation between the two carbenic moieties (such as **A** in Scheme 1),[2, 11, 13] or the introduction of planar fused-aromatic groups between the two carbene moieties, such as benzene (**B**),[14-15] pyracene (**C**),[16-17] pyrene (**D**),[18-20] perylene (**E**)[21] or quinoxalinophenanthrophenazine (**F**).[22] *Janus*-type benzobisoxazolin-2-ylidene ligands[23] and dianionic bis(malonate-NHCs)[15, 24] have also been prepared for this purpose.

All these ligands have allowed establishing fixed distances between the metals ranging from 6 to 24 Å. The presence of the bridging polyaromatic moieties also introduce important features in the catalytic properties of the complexes, due to supramolecular interactions (mostly due to $\pi-\pi$-stacking interactions) between the polyaromatic ligands and the substrates, and to the self-association of the catalysts.[25] Not less important is that the presence of the polyaromatic moieties provides new photophysical properties to the complexes (mainly fluorescence), thus affording an interesting approach to combine them with the intrinsic features of transition metals. In this regard, several mono-NHCs containing an annulated polyaromatic backbone have been synthesized (Scheme 2) and coordinated to transition metals furnishing new complexes with very interesting photophysical properties.[18, 26-33]

In this work, we aimed to prepare a family of palladium complexes that combine pyrene-based mono- and bis-NHC ligands with benzimidazolylidenes. We thought that providing an efficient route for combining mono-NHC ligands with bis-NHC ligands would provide new examples of complexes decorated with aromatic fragments. Other mononuclear palladium complexes that contain two NHCs with different type of annulated polyaromatic groups,
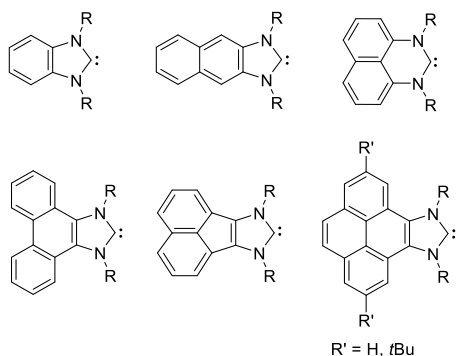
namely benzimidazolylidene and benzoxazolinylidene ligands, are described in the literature.[23]

Scheme 2. Selected examples of mono-NHC ligands decorated with polyaromatic backbones

Results and Discussion

Synthesis and Characterization. For the preparation of our complexes with mixed aromatic-NHC ligands, we thought that a good strategy would be to use halide-bridged palladium (II) dinuclear complexes, since the addition of an L type ligand should provide direct access to the desired products. Our palladium-benzimidazolylidene complexes were obtained following the procedure depicted in Scheme 3,[34] which involves the reaction of the benzimidazolium salts **A** (**A-Et** or **A-nPr**) with Pd(OAc)$_2$ in the presence of NaBr. This procedure allowed the isolation of the desired complexes in excellent yields (85 and 77% yield for **1-Et** and **1-nPr**, respectively). Complexes of type **1** were characterized by NMR spectroscopy, mass spectrometry and gave satisfactory elemental analysis. Mass spectrometry provided evidence of the dinuclear nature of these compounds, as the prominent peak corresponds to [M−Br+MeCN]$^+$ species. The ^{13}C NMR spectra show the distinctive signals due to the metallated carbene carbon (157.3 and 157.7 ppm for **1-Et** and **1-nPr**, respectively).
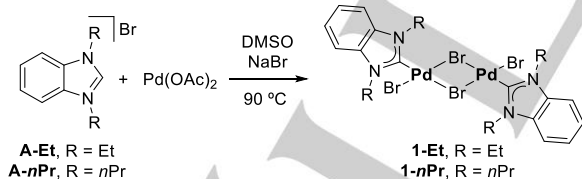
Scheme 3. Synthesis of complexes **1**

The molecular structure of complex **1-Et** was unambiguously confirmed by single crystal X-ray diffraction studies (Figure 1). The molecule consists of a dinuclear palladium complex, in which each palladium center is coordinated to one benzimidazolylidene ligand. One terminal bromide and two bridging bromide ligand complete the pseudo-square planar coordination sphere about each metal fragment. As expected, the Pd1–Br2 bond distance,

trans to the NHC ligand, is longer than that observed for the other type of Pd–Br bonds of the molecule due to the strong *trans* influence of the NHC ligand. The coordination planes of the two palladium centers are not coplanar (the angle between them is 13.76(7)⁰), providing a slightly bent structure (Figure 1, bottom). The angle between the planes defined by the two benzimidazolylidene ligands is 32.0(2)⁰. These two structural features are in contrast with molecular structures of similar type of dinuclear complexes based on NHCs of Pd[34-35] or Rh,[36] in which the coordination planes of the metal center are coplanar and the planes defined by the NHC ligands are parallel. We think that the relative small size of the N-Et groups at the NHC, compared with the N-substituents present in related complexes (dipp, *i*Pr and Bn), makes the environment around the metal center less sterically constrained, thus allowing a higher degree of rotation to the ligands. The angle between the coordination plane of the palladium center and the plane defined by the azole ring is 79.33(12)⁰. The Pd–C$_{carbene}$ distance is 1.955(5) Å and the distance between the two palladium centers is 3.5778(7) Å. The crystal packing of **1-Et** reveals π−π stacking interactions between pairs of dinuclear complexes, located a distance of 3.501 Å. The CCDC reference number for complex **1-Et** was assigned as 1921386.
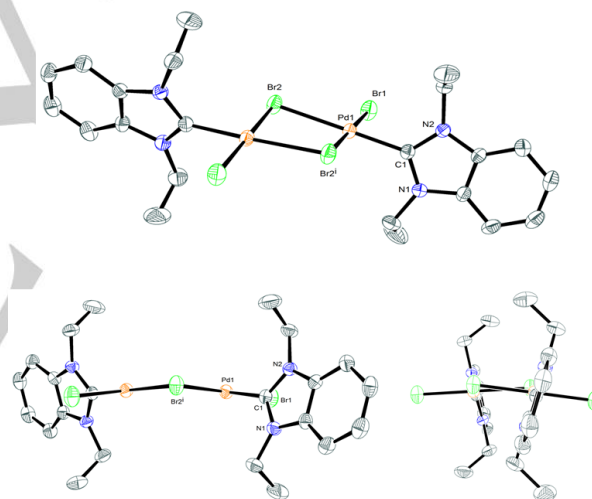

Figure 1. Different perspectives of the molecular structure of **1-Et**. Hydrogen atoms and solvent (CHCl$_3$) omitted for clarity. Thermal ellipsoids are shown at the 50 % level of probability. Selected bond distances (angstroms) and angles (degrees): Pd1–C1 1.955(5), Pd1–Br1 2.4160(6), Pd1–Br2 2.5289(6), Pd1–Br2^i 2.4478(6), C1–Pd1–Br2 177.01(14), Br1–Pd1–Br2^i 179.84(2), C1–Pd1–Br1 89.93(14), Br2–Pd1–Br2^i 87.17(2).

Dinuclear Pd(II)-NHC complexes have proved to be excellent precursors for the synthesis of a range of monocarbene complexes.[34-35, 37] In our case, we used complexes **1** in combination with our previously reported pyrene-based mono- and bis-NHCs for preparing new palladium complexes containing two types of NHC ligands decorated with aromatic moieties.

Mono-palladium complexes **2** were synthesized through a transmetallation strategy (Scheme 4).[38] Silver-carbene complexes based on pyrene were generated *in situ* by treating the mono-azolium salts (**B**)[39] with Ag$_2$O. Transmetallation by addition of the palladium dinuclear complexes (**1**) provided the desired mono-palladium complexes (**2**) in good yields after purification by column chromatography.
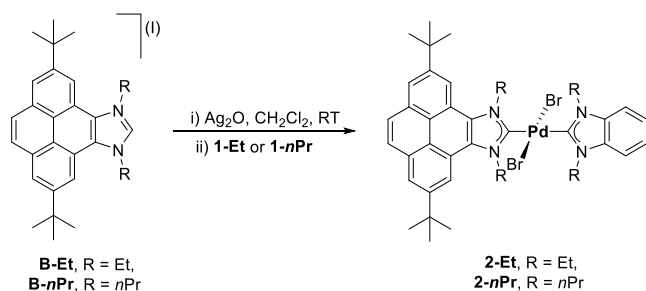
Scheme 4. Synthesis of monometallic complexes **2**

The isolation of the di-palladium complexes **3** was better achieved by means of a deprotonation route (Scheme 5). The reaction of the pyrene-based bis-imidazolium salts (**C**)[19] with the palladium dinuclear complexes (**1**) in the presence of KO*t*Bu yielded the dimetallic complexes **3**, which were isolated as yellow powders after purification by column chromatography. Complexes of type **2** and **3** were characterized by means of mass spectrometry, NMR spectroscopy, and gave satisfactory elemental analysis.
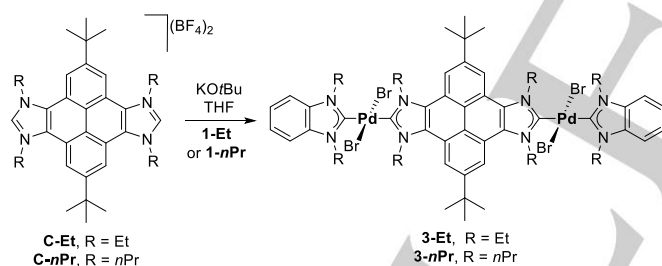
Scheme 5. Synthesis of complexes **2** and **3**

The ^{1}H NMR spectrum of the monometallic complexes **2** is consistent with their expected two-fold symmetry, as exemplified by the equivalence of the signals corresponding to the protons of the pyrene fragment. Interestingly, from the two possible isomers (*cis* or *trans*) the *trans* one was obtained selectively. This is evident from ^{1}H NMR spectroscopy, as the protons of the N-CH$_2$ groups are equivalent for each carbene ligand, while they should be diasterotopic for the *cis* isomer.

The ^{1}H NMR spectra of the dimetallic complexes **3** indicates the formation of compounds with highly symmetric structures, as only one resonance is observed for the four aromatic protons of the pyrene fragment. No diastereotopicity is observed for the signals

corresponding to the protons of the N-CH$_2$ groups, thus the formation of *cis* isomers can be ruled out.

Another indication that the two different NHCs are mutually *trans* in complexes **2** and **3** arises from the ^{13}C NMR spectra, as the resonances due to the two metallated carbene atoms appear at 181.2-181.0 and 178.8-176.6 ppm, in the typical region shown for *trans*-bis-NHC complexes of the type PdX$_2$(NHC)$_2$[40] (*cis*-NHCs appear at higher fields, ~170 ppm).[41]

The ^{13}C$_{carbene}$ NMR signal of the 1,3-diisopropylbenzimidazolylidene (*i*Pr$_2$-bimy) ligand (so-called HEP value) in complexes of the type *trans*-[PdBr$_2$(*i*Pr$_2$-bimy)(NHC)] and [Pd$_2$Br$_4$(*i*Pr-bimy)$_2$(diNHC)] has been proposed by Huyhn and co-workers for the evaluation of the donor strength of *trans*-standing mono-NHC[42] and dicarbene-bridged ligands,[43] respectively. Strong donating ligands induce downfield shifts while weaker donating ones would lead to higher field HEP signals.

Complexes **2** and **3** differ from the proposed probes in that they contain either 1,3-di-ethylbenzimidazolylidene (Et$_2$-bimy) or 1,3-di-*n*-propylbenzimidazolylidene (*n*Pr$_2$-bimy) ligands instead of the *i*Pr$_2$-bimy reporter ligand. Using our benzimidazolylidene-based ligands as probes, we can observe that there is a very small difference between the ^{13}C$_{carbene}$ NMR signals for these ligands in **2** (181.2 ppm) and **3** (181.0 ppm). This very small difference might indicate that the pyrene-based mono- and bis-NHC ligands have very similar electron-donating character, which is in agreement with our previous findings using other methodologies.

The molecular structure of complex **3-Et** was confirmed by single crystal X-ray diffraction studies (Figure 2). The molecule consists of a pyrene-based bis-imidazolylidene ligand connecting two palladium centers that complete their coordination sphere with two (*trans*) bromide ligands and a benzimidazolylidene ligand. The planes defined by the benzimidazolylidene ligand and by the pyrene moiety are quasi-coplanar (3.59(9)⁰), and quasi-perpendicular to the coordination plane of the palladium center, with dihedral angles of 85.57(12)⁰ and 89.02(14)⁰. The Pd1–C1 and the Pd1–C2 bond distances are 2.023(4) Å and 2.018(4) Å, respectively, in agreement with bond distances reported for palladium complexes containing two NHC ligands in a relative *trans* fashion.[41]

The through space Pd–Pd distance is 13.1848(6) Å, in the range of those observed for Rh,[19] Ir,[19] Ru[18] and Pt[20, 44] homo-bimetallic complexes supported by the pyrene-bis-imidazolylidene ligand. In contrast with the previous complexes bearing pyrene-based NHC ligand, the crystal structure does not show intermolecular π–π stacking interactions **3-Et**. The CCDC reference number for complex **3-Et** was assigned as 1921387.

The photophysical properties of the metal complexes **1**, **2** and **3-Et** were studied in dichloromethane solution at 298 K. The palladium dinuclear complexes **1** show almost superimposable absorption spectra with λ$_{max}$ at 255, 291 and 349 nm (see Figure S1 in the Supporting Information), and exhibit negligible fluorescence emission.

Complexes **2** and **3-Et** exhibit an intense absorption band with λ$_{max}$ at 245 nm. The bis-NHC complex **3-Et** also exhibits a less intense vibronic-structured band at 320-360 nm, which can be assigned to pyrene-centered transitions (see Figure S2 in the

Supporting Information). Complexes **2** and **3-Et** featured vibronically resolved bands in their emission spectra but exhibit very low fluorescence emission under the conditions we performed the studies.
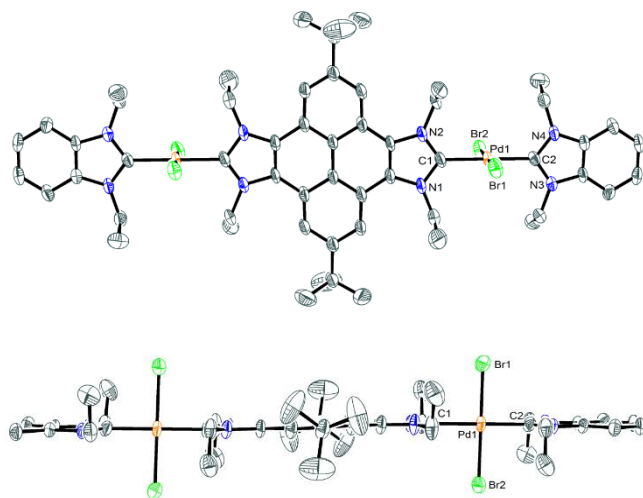
Figure 2. Two perspectives of the molecular structure of **3-Et**. Hydrogen atoms and solvent (CHCl₃) omitted for clarity. Thermal ellipsoids are shown at the 50 % level of probability. Selected bond distances (angstroms) and angles (degrees): Pd1–C1 2.023(4), Pd1–C2 2.018(4), Pd1–Br1 2.4214(6), Pd1–Br2 2.4315(6), C1–Pd1-C2 179.68(19), Br1–Pd1–Br2 178.73(2), C1–Pd1–Br1 91.37(14), C2–Pd1–Br2 91.64(13).

Conclusions

In summary, we have reported the synthesis and characterization of a new family of mono- and dimetallic palladium complexes bearing two types of NHCs differing in the size of the aromatic annulated backbone. Geometrical isomers locating the two NHCs in a relative *trans* configuration were obtained selectively, avoiding the generation of other potential isomers. We think that with this work we provided an efficient route for the *trans*-selective preparation of palladium complexes with two different types of NHC ligands. We think that this synthetic procedure will improve the chances to obtain NHC-based complexes with interesting photophysical properties by, for instance, extending it to Pt(II) complexes.

Experimental Section

General methods. The imidazolium salt **A-Et**,[45] **B-Et**,[39] **B-*n*Pr**,[39] **C-Et**[19] and **C-*n*Pr**[19] were prepared as previously reported. All operations were carried out by using standard Schlenk techniques under nitrogen atmosphere unless otherwise stated. Anhydrous solvents were dried using a solvent purification system (SPS M BRAUN) or purchased from Aldrich and degassed prior to be used by purging with nitrogen and kept over molecular sieves. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on a Bruker 300 or 400

MHz, or in a Varian Innova 500 MHz, using CDCl₃ or DMSO-*d₆* as solvents. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. Exact mass analysis was realized using Q-TOF premier mass spectrometer with electrospray source (Waters, Manchester, UK) operating at a resolution of ca. 16 000 (fwhm). Elemental analyses were carried out on a TruSpec Micro Series. UV-Visible absorption spectra were recorded on a Varian Cary 300 BIO spectrophotometer using dichloromethane under ambient conditions. Emission spectra were recorded on a modular Horiba FluoroLog-3 spectrofluorometer employing dichloromethane.

Synthesis of A-*n*Pr. A thick-walled Schlenk tube fitted with a Teflon cap was charged with benzimidazole (424 mg, 3.52 mmol), NaHCO₃ (606.4 mg, 7.22 mmol) and acetonitrile (5 mL). The mixture was stirred at 90 ºC during 1 h. After that, *n*-propylbromide (1.93 mL, 21 mmol) was added at room temperature and the mixture was further heated at 90 ºC overnight. The solvent was removed under vacuum. The brownish solid residue was suspended in CH₂Cl₂ and filtered to remove insoluble inorganic salts. Precipitation of the filtrate with a mixture CH₂Cl₂/diethyl ether afforded compound **A-*n*Pr** as a white solid. Yield: 990 mg, 99 %. ¹H NMR (300 MHz, dmso-*d₆*): δ 10.00 (s, 1H, NC*H*N), 8.13 (dd, $^3J_{H-H}$ = 6.2 Hz, $^4J_{H-H}$ = 3.1 Hz, 2H, C*H*ₐᵣₒₘ), 7.69 (dd, $^3J_{H-H}$ = 6.3 Hz, $^4J_{H-H}$ = 3.1 Hz, 2H, C*H*ₐᵣₒₘ), 4.50 (t, $^3J_{H-H}$ = 7.1 Hz, 4H, NC*H₂*CH₂CH₃), 2.01-1.89 (m, 4H, NCH₂C*H₂*CH₃), 0.92 (t, $^3J_{H-H}$ = 7.4 Hz, 6H, NCH₂CH₂C*H₃*). ¹³C NMR (75 MHz, dmso-*d₆*): δ 142.1 (NCHN), 131.1 (*C*q), 126.4 (C*H*ₐᵣₒₘ), 113.7 (C*H*ₐᵣₒₘ), 48.0 (NC*H₂*CH₂CH₃), 22.0 (NCH₂*C*H₂CH₃), 10.6 (NCH₂CH₂*C*H₃). Anal. Calc. for N₂C₁₃H₁₉Br·H₂O (301.22): C, 51.83; H, 7.03; N, 9.30. Found: C, 51.38; H, 7.18; N, 8.99. Electrospray MS (20 V, m/z): 203.3 [M]⁺.

General procedure for the synthesis of palladium dinuclear complexes 1. Pd(OAc)₂ (397 mg, 1.77 mmol, 1 equiv.), NaBr (865 mg, 7.08 mmol, 4 equiv.) and the corresponding imidazolium salt (1.77 mmol, 1 equiv.) were dissolved in 7 mL of DMSO and the mixture was stirred at 90 ºC during 24 h. Then, the solvent was removed under vacuum. The solid residue was dissolved in CH₂Cl₂ (300 mL) and the solution was washed with water (4 × 200 mL). The organic phase was dried with MgSO₄, filtered and the solvent was removed under vacuum. Precipitation from a mixture CH₂Cl₂/hexane afforded the corresponding complex as an orange solid.

Synthesis of 1-Et. Yield: 732 mg, 85 %. ¹H NMR (300 MHz, DMSO-*d₆*): δ 7.73 (dd, $^3J_{H-H}$ = 6.0, $^4J_{H-H}$ = 3.1 Hz, 4H, C*H*ₐᵣₒₘ), 7.36 (dd, $^3J_{H-H}$ = 6.1 Hz, $^4J_{H-H}$ = 3.1 Hz, 4H, C*H*ₐᵣₒₘ), 4.80 (q, $^3J_{H-H}$ = 7.2 Hz, 8H, NC*H₂*CH₃), 1.56 (t, $^3J_{H-H}$ = 7.2 Hz, 12H, NCH₂C*H₃*). ¹³C NMR (75 MHz, dmso-*d₆*): δ 157.3 (Pd-*C*carbene), 133.3 (*C*q), 123.2 (C*H*ₐᵣₒₘ), 110.8 (C*H*ₐᵣₒₘ), 43.1 (N*C*H₂CH₃), 14.0 (NCH₂*C*H₃). Anal. Calc. for Pd₂Br₄N₄C₂₂H₂₈ (880.95): C, 30.00; H, 3.20; N, 6.36. Found: C, 29.79; H, 3.65; N, 6.26. Electrospray MS (20 V, *m/z*): 842.0 [M−Br+MeCN]⁺.

Synthesis of 1-*n*Pr. Yield: 634 mg, 77 %. ¹H NMR (500 MHz, DMSO-*d₆*): δ 7.73 (dd, $^3J_{H-H}$ = 6.0 Hz, $^4J_{H-H}$ = 3.0 Hz, 4H, C*H*ₐᵣₒₘ), 7.34 (dd, $^3J_{H-H}$ = 6.0 Hz, $^4J_{H-H}$ = 3.0 Hz, 4H, C*H*ₐᵣₒₘ), 4.78-4.57 (m, 8H, NC*H₂*CH₂CH₃), 2.16-2.08 (m, 8H, NCH₂C*H₂*CH₃), 1.01 (t, $^3J_{H-H}$ = 7.3 Hz, 12H, NCH₂CH₂C*H₃*). ¹³C NMR (75 MHz, dmso-*d₆*): δ 157.7 (Pd-*C*carbene), 133.8 (*C*q), 123.1 (C*H*ₐᵣₒₘ), 110.9 (C*H*ₐᵣₒₘ), 49.4 (N*C*H₂CH₂CH₃), 22.0 (NCH₂*C*H₂CH₃), 11.2 (NCH₂CH₂*C*H₃). Anal. Calc. for Pd₂Br₄N₄C₂₆H₃₄·7H₂O (1061.15): C, 29.43; H, 4.56; N, 5.28. Found: C, 29.21; H, 4.34; N, 5.34. Electrospray MS (20 V, *m/z*): 898.1 [M−Br+MeCN]⁺.

General procedure for the synthesis of complexes 2. A suspension of the corresponding mono-imidazolium salt (2 equiv.) and Ag₂O (1 equiv.) in CH₂Cl₂ (15 mL) was stirred at room temperature for 2 h under the exclusion of light. Then **1** was added (1 equiv.) and the resulting mixture was stirred

at room temperature for 2 h. The suspension was filtered through a pad of Celite and the solvent removed under vacuum. The crude solid was purified by column chromatography. Elution with a 1:1 mixture dichloromethane/hexane afforded the separation of a yellow band that contained complex **2-Et** (or **2-nPr**). The desired complex was isolated as a yellow solid after precipitation in a mixture of dichloromethane/pentane.

Synthesis of 2-Et. The reaction was carried out with **B-Et** (70 mg, 0.13 mmol), Ag_2O (15.2 mg, 0.065 mmol) and **1-Et** (57 mg, 0.065 mmol). Yield: 55 mg, 50 %. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.75 (d, $^4J_{H-H}$ = 1.6 Hz, 2H, CH_{pyr}), 8.20 (d, $^4J_{H-H}$ = 1.6 Hz, 2H, CH_{pyr}), 8.06 (s, 2H, CH_{pyr}), 7.45 (dd, $^3J_{H-H}$ = 6.0, $^3J_{H-H}$ = 3.1 Hz, 2H, CH_{arom}), 7.31 (dd, $^3J_{H-H}$ = 6.0, $^3J_{H-H}$ = 3.0 Hz, 2H, CH_{arom}), 5.73 (q, $^3J_{H-H}$ = 7.1 Hz, 4H, NCH_2CH$_3$), 5.01 (q, $^3J_{H-H}$ = 7.3 Hz, 4H, NCH_2CH$_3$), 2.07 (t, $^3J_{H-H}$ = 7.3 Hz, 6H, NCH$_2$CH_3), 1.86 (t, $^3J_{H-H}$ = 7.3 Hz, 6H, NCH$_2$CH_3), 1.63 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (126 MHz, CDCl$_3$): δ 181.2 (Pd-$C_{carbene}$), 176.7 (Pd-$C_{carbene}$), 148.8 ($C_{q\ pyr}$), 134.3 (C_q), 131.7 ($C_{q\ pyr}$), 128.7 ($C_{q\ pyr}$), 128.2 (CH_{pyr}), 122.6 (CH_{arom}), 122.1 (CH_{pyr}), 121.0 ($C_{q\ pyr}$), 120.8 ($C_{q\ pyr}$), 116.5 (CH_{pyr}), 110.2 (CH_{arom}), 46.7 (NCH$_2$CH$_3$), 43.3 (NCH$_2$CH$_3$), 35.4 (C(CH$_3$)$_3$), 31.9 (C(CH$_3$)$_3$), 15.0 (NCH$_2$$CH_3$), 14.9 (NCH$_2$$CH_3$). Anal. Calc. for PdBr$_2N_4C_{40}H_{48}$ (851.08): C, 56.05; H, 5.69; N, 6.58. Found: C, 56.65; H, 5.45; N, 6.43. Electrospray MS (20 V, m/z): 810.0 [M-Br+CH$_3$CN]$^+$.

Synthesis of 2-nPr. The reaction was carried out with **B-nPr** (136 mg, 0.24 mmol), Ag_2O (28.2 mg, 0.12 mmol) and **1-nPr** (112.4 mg, 0.12 mmol). Yield: 125 mg, 57 %. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.67 (d, $^4J_{H-H}$ = 1.6 Hz, 2H, CH_{pyr}), 8.20 (d, $^4J_{H-H}$ = 1.6 Hz, 2H, CH_{pyr}), 8.06 (s, 2H, CH_{pyr}), 7.45 (dd, $^3J_{H-H}$ = 6.0, $^3J_{H-H}$ = 3.1 Hz, 2H, CH_{arom}), 7.29 (dd, $^3J_{H-H}$ = 6.0, $^3J_{H-H}$ = 3.0 Hz, 2H, CH_{arom}), 5.60-5.56 (m, 4H, NCH_2CH$_2$CH$_3$), 4.92-4.98 (m, 4H, NCH_2CH$_2$CH$_3$), 2.55-2.49 (m, 4H, NCH$_2$CH_2CH$_3$), 2.41-2.36 (m, 4H, NCH$_2$CH_2CH$_3$), 1.63 (s, 18H, C(CH_3)$_3$), 1.40 (t, $^3J_{H-H}$ = 7.2 Hz, 6H, NCH$_2$CH$_2$CH_3), 1.23 (t, $^3J_{H-H}$ = 7.2 Hz, 6H, NCH$_2$CH$_2$CH_3). ^{13}C NMR (126 MHz, CDCl$_3$): δ 181.2 (Pd-$C_{carbene}$), 176.5 (Pd-$C_{carbene}$), 148.8 ($C_{q\ pyr}$), 134.9 (C_q), 131.8 ($C_{q\ pyr}$), 128.9 ($C_{q\ pyr}$), 128.3 (CH_{pyr}), 122.8 (CH_{arom}), 122.3 (CH_{pyr}), 121.2 ($C_{q\ pyr}$), 121.0 ($C_{q\ pyr}$), 116.6 (CH_{pyr}), 110.6 (CH_{arom}), 53.7 (NCH$_2$CH$_2$CH$_3$), 50.2 (NCH$_2$CH$_2$CH$_3$), 35.5 (C(CH$_3$)$_3$), 32.0 (C(CH$_3$)$_3$), 23.4 (NCH$_2$$CH_2CH_3$), 23.2 (NCH$_2$$CH_2CH_3$), 12.2 (NCH$_2CH_2$$CH_3$), 11.98 (NCH$_2CH_2$$CH_3$). Anal. Calc. for PdBr$_2N_4C_{44}H_{56}$ (907.19): C, 58.26; H, 6.22; N, 6.18. Found: C, 58.16; H, 6.81; N, 5.51. Electrospray MS (20 V, m/z): 866.3 [M-Br+CH$_3$CN]$^+$.

General procedure for the synthesis of complexes 3. The corresponding bis-imidazolium salt (1 equiv.), the metal precursor **2** (1 equiv.) and KOtBu (2.2 equiv.) were suspended in THF and the reaction was stirred at room temperature overnight. The mixture was filtered through Celite. The solution was concentrated under reduced pressure and the solid was purified by the appropriate methodology.

Synthesis of 3-Et. The reaction was carried out using **C-Et** (77.4 mg, 0.114 mmol), **1-Et** (100 mg, 0.114 mmol) and KOtBu (29.5 mg, 0.25 mmol). The crude was purified by column chromatography. Elution with a mixture 9:1 dichloromethane/hexane afforded the separation of a yellow band that contained compound **3-Et**. The desired complex was isolated as a yellow solid after precipitation in a mixture dichloromethane/hexane. Yield: 27 mg, 19 %. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.82 (s, 4H, CH_{pyr}, 4H), 7.45 (br s, 4H, CH_{arom}), 7.32 (br s, 4H, CH_{arom}), 5.77 (q, $^3J_{H-H}$ = 6.5 Hz, 8H, NCH_2CH$_3$), 5.01 (q, $^3J_{H-H}$ = 6.7 Hz, 8H, NCH_2CH$_3$), 2.10 (t, $^3J_{H-H}$ = 6.5 Hz, 12H, NCH$_2$CH_3), 1.86 (t, $^3J_{H-H}$ = 6.7 Hz, 12H, NCH$_2$CH_3), 1.68 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 181.0 (Pd-$C_{carbene}$), 178.8 (Pd-$C_{carbene}$), 149.2 ($C_{q\ pyr}$), 134.5 (C_q), 129.0 ($C_{q\ pyr}$), 122.9 (CH_{arom}), 121.7 ($C_{q\ pyr}$), 119.2 ($C_{q\ pyr}$), 116.2 (CH_{pyr}), 110.4 (CH_{arom}), 47.2 (NCH$_2$CH$_3$), 43.5 (NCH$_2$CH$_3$), 35.9 (C(CH$_3$)$_3$), 31.9 (C(CH$_3$)$_3$), 15.2 (NCH$_2$$CH_3$), 15.1 (NCH$_2$$CH_3$). Anal. Calc. for Pd$_2Br_4N_8C_{56}H_{70}$·2H$_2$O (1423.72): C, 47.24; H, 5.24; N, 7.87. Found: C,

47.05.14; H, 5.21; N, 7.46. Electrospray MS (20 V, m/z): 1350.0 [M-Br+MeCN]$^+$.

Synthesis of 3-nPr. The reaction was carried out using **C-nPr** (78.8 mg, 0.107 mmol), **1-nPr** (100 mg, 0.107 mmol) and KOtBu (27.8 mg, 0.24 mmol). Precipitation with a mixture CH$_2$Cl$_2$/hexane afforded compound **3-nPr** as a yellow solid. Yield: 100 mg, 62 %. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.74 (s, 4H, CH_{pyr}), 7.45 (dd, $^3J_{H-H}$ = 6.0 Hz, $^4J_{H-H}$ = 3.1 Hz, 4H, CH_{arom}), 7.30 (dd, $^3J_{H-H}$ = 6.0 Hz, $^3J_{H-H}$ = 3.1 Hz, 4H, CH_{arom}), 5.64-5.60 (m, 8H, N-CH_2-CH$_2$-CH$_3$), 4.92-4.89 (m, 8H, N-CH_2-CH$_2$-CH$_3$), 2.57-2.49 (m, 8H, N-CH$_2$-CH_2-CH$_3$), 2.42-2.35 (m, 8H, N-CH$_2$-CH_2-CH$_3$), 1.68 (s, 18H, C(CH_3)$_3$), 1.41 (t, $^3J_{H-H}$ = 7.4 Hz, 12H, N-CH$_2$-CH$_2$-CH_3), 1.23 (t, $^3J_{H-H}$ = 7.4 Hz, 12H, N-CH$_2$-CH$_2$-CH_3). ^{13}C NMR (126 MHz, CDCl$_3$): δ 181.0 (Pd-$C_{carbene}$), 178.6 (Pd-$C_{carbene}$), 149.0 ($C_{q\ pyr}$), 135.0 (C_q), 129.1 ($C_{q\ pyr}$), 122.8 (CH_{arom}), 121.8 ($C_{q\ pyr}$), 119.3 ($C_{q\ pyr}$), 116.2 (CH_{pyr}), 110.7 (CH_{arom}), 54.0 (NCH$_2$CH$_2$CH$_3$), 50.3 (NCH$_2$CH$_2$CH$_3$), 35.8 (C(CH$_3$)$_3$), 32.0 (C(CH$_3$)$_3$), 23.4 (NCH$_2$$CH_2CH_3$), 23.2 (NCH$_2$$CH_2CH_3$), 12.20 (NCH$_2CH_2$$CH_3$), 11.7 (NCH$_2CH_2$$CH_3$). Anal. Calc. for Pd$_2Br_4N_8C_{64}H_{86}$·2H$_2$O (1535.93): C, 50.05; H, 5.91; N, 7.30. Found: C, 50.14; H, 5.40; N, 6.87. Electrospray MS (20 V, m/z): 1460.3 [M-Br+MeCN]$^+$.

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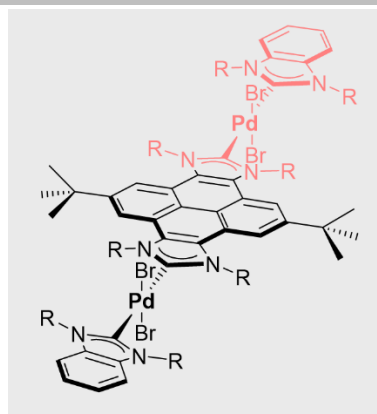
Combining aromatic NHC ligands

Sergio Gonell,* Eduardo Peris, and Macarena Poyatos*

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Structural features of mono and dimetallic complexes of palladium combining two types of aromatic NHC ligands

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