

Silver and palladium complexes of a bis(benzimidazolin-2-ylidene)pyridine pincer ligand

David H. Brown,^{*,†} Gareth L. Nealon,[†] Peter V. Simpson,[‡] Brian W. Skelton[‡] and Zhisen Wang[†]

*Nanochemistry Research Institute, Department of Applied Chemistry, Curtin University of Technology,
GPO Box U1987, Perth WA 6845, Australia, and Chemistry M313, School of Biomedical,
Biomolecular and Chemical Sciences, The University of Western Australia, Crawley, WA 6009,
Australia*

*To whom correspondence should be addressed. E-mail: d.h.brown@curtin.edu.au. Tel: +61 8 9266 1279. Fax: +61 8 9266 4699.

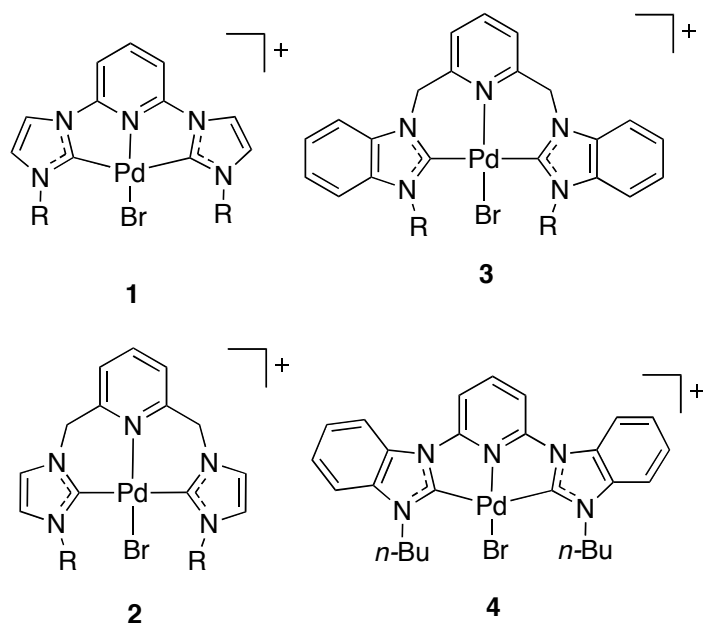
[†] Curtin University of Technology

[‡] The University of Western Australia

Summary: Reaction of 2,6-bis(3-butylbenzimidazol-1-ium)pyridine dibromide with silver oxide affords a dinuclear complex of the type $[L_2Ag_2]^{2+}$ [$L = 2,6$ -bis(3-butylbenzimidazolin-2-ylidene)pyridine]. 1H NMR spectroscopic studies suggest that the dinuclear structure is also present in solution. Transmetalation of the silver-NHC complex with $PdCl_2(CH_3CN)_2$ yields a mononuclear palladium complex of the type $[LPdCl]^+$, with a chelating C,N,C -pincer ligand.

N-Heterocyclic carbenes (NHCs) and their metal complexes are prevalent in modern organometallic chemistry.¹ One of the main areas of investigation of these systems involves the use of NHCs as ligands in metal-center mediated catalytic reactions.² Studies involving NHCs are, in general, dominated by NHCs based on the imidazole ring.^{3,4} Benzimidazolin-2-ylidenes have received considerably less interest though in recent years this area has been developed by a number of groups.^{5,6}

One class of NHC ligands that has attracted significant attention to-date is that of the *C,N,C* pyridine-based pincer-ligands (e.g. ligands in **1** and **2**).^{3,4} Within this class, the bis(imidazolinylidene)-2,6-pyridine ligands (as in **1**) have been extensively investigated with a wide range of transition metals (e.g. Cr, Fe, Ru, Rh, Pd, Ni, Ti).³ The complexes **1** and **2** have been of interest because of their application as pre-catalysts in coupling reactions. Complex **1** displays high activity in Heck reactions, including significant activity with the typically unreactive aryl chlorides.^{7,8} Complexes of benzimidazolin-2-ylidene *C,N,C* pyridine-based pincer ligands are relatively unexplored and have, until recently, only been reported with a lutidinediyl structure (e.g. **3**).⁹ During the study reported here, Dötz and co-workers reported the synthesis and catalytic activity of **4** — the first metal complex of a bis(benzimidazolin-2-ylidene)-pyridine pincer with a 2,6-pyridine core.¹⁰

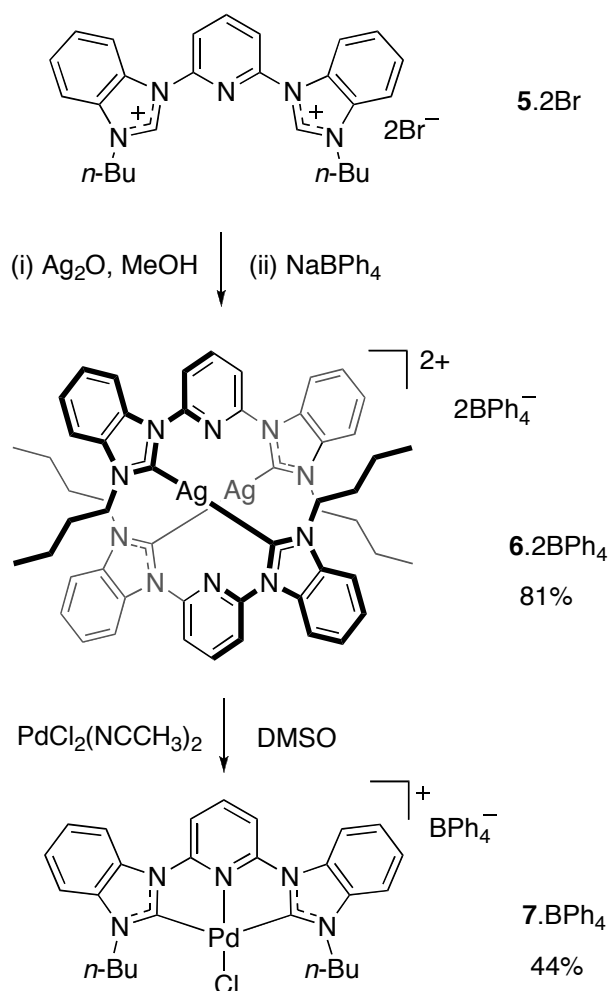


Results and Discussion

The benzimidazolium salt **5.2Br** was prepared by the alkylation of 2,6-di(benzimidazolyl)pyridine with excess 1-bromobutane in DMF. 2,6-Di(benzimidazolyl)pyridine was conveniently prepared by the reaction of sodium benzimidazolate with 2,6-dichloropyridine in DMF, initially at room temperature, then at 60 °C and finally heating at 140 °C, without using a sealed reactor. See Supporting Information for the synthesis and characterization of **5.2Br** and di(benzimidazolyl)pyridine, and some further discussion.

The reaction of **5.2Br** with silver(I) oxide in methanol, followed by filtration (to remove AgBr) and subsequent precipitation by the addition of a solution of sodium tetraphenylborate afforded the dinuclear silver complex **6.2BPh₄** in 81% yield (Scheme 1). Precipitation with tetraphenylborate allows the facile isolation of **6.2BPh₄**. Attempts at isolating a product, such as **6.2Br**, directly from the reaction mixture was not successful.

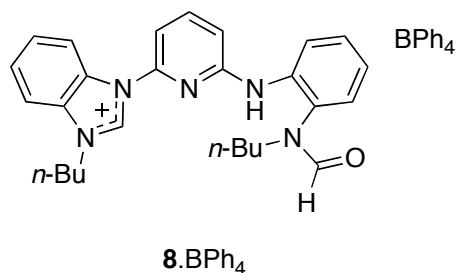
Scheme 1. Synthesis of 6.2BPh₄ and 7.BPh₄



Single crystal X-ray crystallographic studies indicate that, in the solid-state, complex **6** exists as a dinuclear silver complex with the twisted structure shown in Scheme 1 (see Figure 1 and **Solid-State studies**). The ¹³C NMR spectrum of a solution of **6.2BPh₄** in DMSO-*d*₆ displays a broad doublet centered at *ca.* 190 ppm (splitting 200 Hz), which is attributed to the carbene carbons bound to a silver center and is consistent with the literature.^{6,11} The ¹H NMR spectroscopic studies of solutions of **6.2BPh₄** suggest that, at least with a tetraphenylborate counter-anion, the dinuclear structure is also present in solution. Of particular interest are the chemical shifts of the signals corresponding to the protons of the butyl chains. The chemical shifts of the signals corresponding to the methylene and

methyl groups of the butyl chains on **6** (δ 3.52, 1.14, 0.93 and 0.54 ppm for CH₂CH₂CH₂CH₃, DMSO-*d*₆) are significantly up-field compared to the analogous signals for either the ligand precursor **5** (δ 4.71, 2.05, 1.48 and 1.02 ppm, DMSO-*d*₆) or the palladium complex **7** (δ 4.80, 1.81, 1.41 and 0.91 ppm, DMSO-*d*₆). The solid-state structure of **6** reveals that the butyl chains are in a position such that they could be affected by magnetic shielding from the aromatic groups (pyridyl, benzo or imidazolyl) of the opposing ligand in the dinuclear structure [*e.g.* see C(8) in Figure 2]. Such shielding would cause an up-field shift of signals in the ¹H NMR spectrum, suggesting that the dinuclear structure of **6** identified in the solid-state is also present in solution.

During the isolation of **6**.2BPh₄ a small quantity of crystals was isolated from the methanolic filtrate, which were identified as the hydrolysis product **8**.BPh₄ (¹H NMR spectroscopic and X-ray crystallographic studies). Hydrolysis of benzimidazolium cations to afford formanilides (or acetanilides in the case of 2-methylbenzimidazolium cations) has been previously reported in the literature.¹² The formation of the hydrolysis product **8** could be avoided by adding 3Å molecular sieves to the reaction of **5**.2Br with Ag₂O in methanol.



Following the route to Pd-NHC complexes via Ag-NHC transmetallation,¹³ the reaction of the dinuclear silver complex **6**.2BPh₄ with PdCl₂(CH₃CN)₂ in DMSO at room temperature afforded the mononuclear palladium complex **7**, which was isolated as the tetraphenylborate salt **7**.BPh₄ in a 44% yield. The use of other solvents (DMF, acetonitrile, dichloromethane) was unsuccessful. The salt

7.BPh₄ is soluble in organic solvents, presumably aided by the lipophilic counter-anion, and can be readily recrystallised from acetone. The mononuclear structure of **7** was confirmed by crystallographic studies (see Figure 3 and **Solid-State studies**) and the ¹H NMR spectra of solutions of **7**.BPh₄ are consistent with the structure shown.

In the present study, initial attempts to prepare a palladium complex from **5** had focused on the reaction of **5**.2Br with Pd(OAc)₂ in DMF or DMSO under thermal conditions. At low temperatures (60 °C) in DMF the reaction was slow. Moreover, at high temperatures (>150 °C) and prolonged reaction times only complex mixtures were isolated, displaying numerous broad signals in their ¹H NMR spectra. Dötz and co-workers reported the synthesis of **4**.Br by reacting **5**.2Br with Pd(OAc)₂ in DMSO at 160 °C in a microwave reactor for only 25 min.¹⁰ Using similar reaction conditions (**5**.2Br with Pd(OAc)₂ in DMSO, 25 min, 160 °C) but in the absence of microwave radiation was only somewhat more successful, though significant broad signals in the spectrum indicated the formation of species other than **4**.Br. These results would suggest the success of the method reported by Dötz and co-workers depends largely on the use of microwave radiation. The fact that the prolonged reaction times did not afford appreciable quantities of **4** may also indicate that the benzimidazolin-2-ylidene-pincer palladium complexes (e.g. **4**.Br and **7**.BPh₄) may not be as stable as their imidazolin-2-ylidene analogues (e.g. **1** R = Me, Bu).^{7,8} To further investigate the stability of **7**.BPh₄, a solution of the complex in DMSO-*d*₆ was heated at 160 °C in a sealed flask for 1 day. Analysis of the solution by ¹H NMR spectroscopy indicated the presence of additional species (additional sharp and broad signals), though the majority of the complex was still intact, indicating some decomposition had occurred.

Mass spectroscopic studies (low resolution FAB) were conducted on **6**.2BPh₄ and **7**.BPh₄. For **7**.BPh₄, an ion cluster centered near *m/z* 565 is consistent with the mononuclear complex cation **7** (e.g. 564, [L¹⁰⁶Pd³⁵Cl]⁺, 566, [L¹⁰⁸Pd³⁵Cl]⁺). In the case of the dinuclear silver complex **6**.2BPh₄ the spectrum displayed two ion clusters, centered at *m/z* 1063 and 531, which are consistent with the dinuclear cation

plus a hydride (e.g. 1063, $[\text{L}_2^{107}\text{Ag}^{109}\text{Ag} + \text{H}^-]^+$) and a fragment species (e.g. 530, $[\text{L}^{107}\text{Ag}]^+$; and 532 $[\text{L}^{109}\text{Ag}]^+$).

Solid-state studies: The cation of **6** is shown in Figure 1 (see also Supporting Information) and consists of a $[\text{Ag}_2\text{L}_2]^{2+}$ dimer situated on a crystallographic inversion center with the benzimidazolin-2-ylidene groups of each ligand coordinated to two different Ag atoms. The coordination about the Ag atom is essentially linear with the angles around the Ag atoms, C(12)-Ag(1)-C(32') $176.63(6)^\circ$ (' refers to the centrosymmetrically related atom at $-x,-y,1-z$). The Ag...Ag' distance is $3.7848(2)$ Å. The angles between the planes of the pendant groups and the central pyridine of the ligand are $42.57(4)$ and $39.91(4)^\circ$. The Ag to pyridyl nitrogen distances in **6** [Ag(1)-N(21),N(21') $2.984(1)$, $3.012(1)$ Å] are sufficiently long as to indicate only a weak interaction. The structure of **6** is similar to that of the imidazolin-2-ylidene complex **9**, though in **9** the C-Ag-C angles are even more distorted from linearity at $165.5(2)^\circ$, the Ag...Ag distance is much shorter ($3.1585(6)$ Å), but the ligands are much less twisted with central/pendant ring interplanar angles of $21.3(2)$ and $20.6(3)^\circ$ for the two ligands.¹⁴

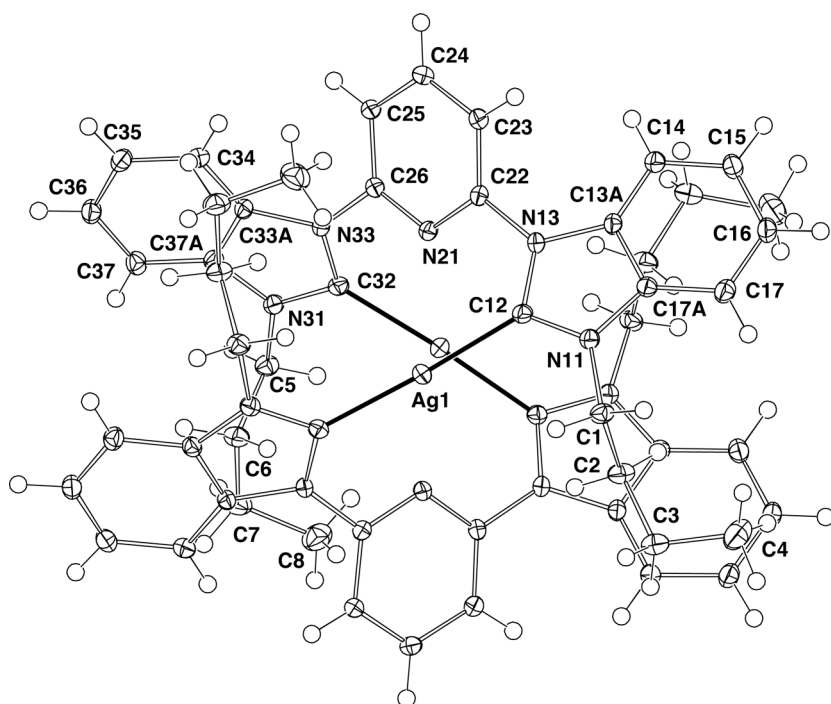
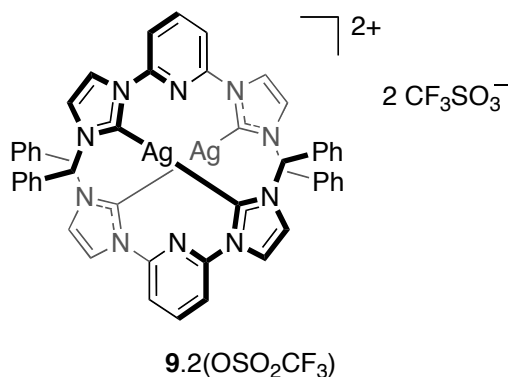


Figure 1. Molecular structure of the cation **6**, projected oblique to the Ag-Ag vector. Ellipsoids have been drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ag(1)-C(12) 2.092(1), C(12)-Ag(1)-C(32') 176.63(6) (' refers to the atom at $-x,-y,1-z$).



The structure of the cation of **7** has a distorted square planar coordination around the central Pd atom (Figure 2). Except for the butyl chains, the atoms are remarkably coplanar with interplanar angles between the pyridyl and the two pendant rings now 5.73(5) and 3.11(6)° and the angle between the 2 pendant rings being 2.68(5)°. This geometry is very similar to that found in the bromo-imidazolyl-2-

ylidene analogues **1.Br** (R = Me, Bu).^{7,8,15} The butyl groups of **7** are directed out of, and are *cis* relative to, the coordination plane. This allows pairing of the cations resulting in a short Pd...Pd distance of 3.6105(2) Å similar to that seen in **1.Br** (R = Bu) of 3.511(18) Å.⁸

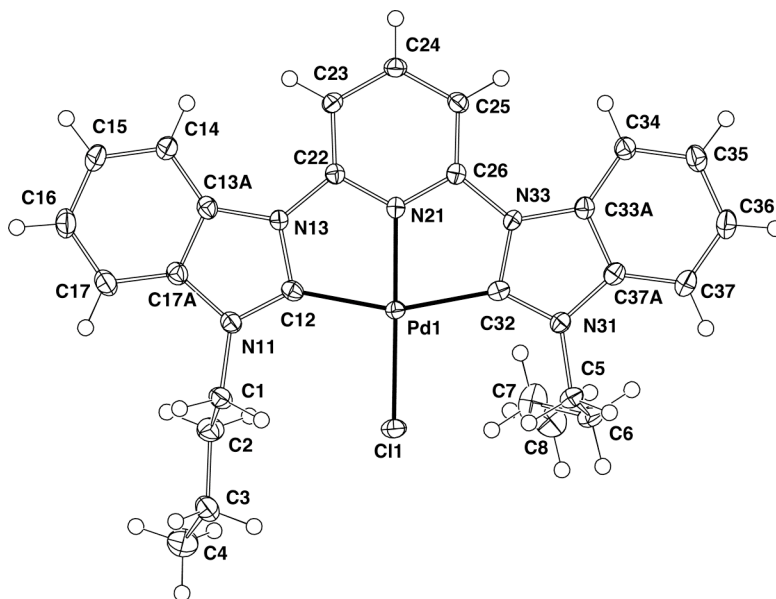


Figure 2. Molecular structure of the cation **7** projected onto the coordination plane. Ellipsoids have been drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pd(1)-N(21) 1.9701(15), Pd(1)-C(12) 2.0202(18), Pd(1)-C(32) 2.0280(18), Pd(1)-Cl(1) 2.2874(5), Pd(1)...Pd(1') 3.6105(2) (' refers to the atom at 1-x,1-y,1-z), N(21)-Pd(1)-C(12) 79.67(7), N(21)-Pd(1)-C(32) 79.29(6), C(12)-Pd(1)-C(32) 158.94(7), N(21)-Pd(1)-Cl(1) 179.42(4), C(12)-Pd(1)-Cl(1) 99.77(5), C(32)-Pd(1)-Cl(1) 101.27(5) .

Conclusion

We have reported the synthesis of a dinuclear bis(benzimidazolin-2-ylidene)-2,6-pyridine-silver complex, of the type $[L_2Ag_2]^{2+}$. ¹H NMR spectroscopic studies suggest that the dinuclear structure identified in the solid-state by X-ray crystallography, was also present in solution. Silver-NHC transmetalation with a palladium(II) source afforded a bis(benzimidazolin-2-ylidene)-2,6-pyridine-palladium complex. An alternative and convenient synthesis of di(benzimidazolyl)-2,6-pyridine is

reported, which avoids the use of a sealed reaction system.

Experimental

General Methods. Nuclear magnetic resonance spectra were recorded using Varian Gemini 200 (200 MHz for ^1H , 50 MHz for ^{13}C), Bruker Avance 500 (500.1 MHz for ^1H , 125.8 MHz for ^{13}C) or Bruker AV-600 MHz (600.13 MHz for ^1H , 150.90 MHz for ^{13}C) spectrometers at ambient temperature. ^1H and ^{13}C chemical shifts were referenced to residual solvent resonances. Microanalyses were performed by the Central Science Laboratory at the University of Tasmania. Mass spectra were obtained by Dr A. Reeder (The University of Western Australia) using a VG Autospec Mass Spectrometer *via* fast atom bombardment (FAB) with a cesium ion source and a *m*-nitrobenzyl alcohol matrix. DMF was dried over 4Å molecular sieves and methanol over 3Å molecular sieves.

Silver complex 6.2BPh₄. A mixture of Ag₂O (0.67 g, 2.89 mmol) and 5.2Br (1 g, 1.71 mmol) in anhydrous methanol (50 mL) was stirred at room temperature, under nitrogen, in the absence of light for 2 d. The mixture was filtered through Celite. A solution of sodium tetraphenylborate (2.3 g, 6.73 mmol) in anhydrous methanol (20 mL) was added to the filtrate. The resulting pink precipitate was collected, washed with hot methanol and recrystallised from hot acetonitrile to afford colourless crystals (1.11g, 81%). Crystals suitable for X-ray diffraction studies were grown by the slow evaporation of an acetonitrile solution of 6.2BPh₄. See Supporting Information for ^1H and ^{13}C NMR data. MS (FAB+): $m/z = 1063$ [M-2BPh₄+H]⁺ (C₅₄H₅₉N₁₀¹⁰⁷Ag¹⁰⁹Ag), 530 (C₂₇H₂₉N₅¹⁰⁷Ag), 532 (C₂₇H₂₉N₅¹⁰⁷Ag). Anal. Calcd for C₁₀₂H₉₈Ag₂B₂N₁₀: C, 72.01; H, 5.81; N, 8.23. Found: C, 71.78; H, 5.81; N, 8.14.

During the synthesis of 6.2BPh₄ the hydrolysis product 8.BPh₄ crystallised from the filtrate of the hot methanol wash. See Supporting Information for compound characterization data and crystallographic data.

Palladium complex 7.BPh₄. A solution of bis(acetonitrile)dichloropalladium(II) (0.027 g, 0.13 mmol) in DMSO (5 mL) was added to a solution of 6.2BPh₄ (0.1 g, 0.06 mmol) in DMSO (10 mL) which was then stirred at room temperature, under nitrogen, in the absence of light for 12 h. The mixture was filtered through Celite and the filtrate was concentrated under reduced pressure. The black oily residue was dissolved in hot acetone (20 mL) and filtered through Celite to afford a clear dark brown solution. Slow evaporation of the acetone solution afforded white crystals and a fine black solid. The solids were collected, washed with cold acetone (3 x 5 mL) and recrystallised from hot acetone to afford light yellow crystals (53 mg, 44%). Crystals suitable for X-ray diffraction studies were grown by the slow evaporation of a solution of the complex in acetone. See Supporting Information for ¹H and ¹³C NMR data. MS (FAB+): $m/z = 564$ [M-BPh₄]⁺ (C₂₇H₂₉N₅¹⁰⁶Pd³⁵Cl), 566 [M-BPh₄]⁺ (C₂₇H₂₉N₅¹⁰⁸Pd³⁵Cl). Anal. Calcd for C₅₁H₄₉BClN₅Pd.2C₃H₆O: C, 68.41; H, 6.14; N, 7.00. Found: C, 68.08; H, 6.01; N, 7.00.

X-ray Structure Determinations. The crystal data for 6.2BPh₄ and 7.BPh₄.2acetone are summarized below with the structures depicted in Figures 1 and 2. The crystal data for 5.2Br and 8.BPh₄ and figures of the structures are provided in Supporting Information. In all figures ellipsoids have been drawn at the 50% probability level. Crystallographic data for the structures were collected at 100(2) K on an Oxford Diffraction Xcalibur (8.BPh₄) or Gemini (5.2Br, 6.2BPh₄, 7.BPh₄.2acetone) diffractometer fitted with graphite-monochromated Mo K α radiation yielding N_{total} reflections, these merging to N unique after multiscan absorption correction (R_{int} cited), with N_0 reflections with $I > 3\sigma(I)$. The structures were refined against F^2 with full-matrix least-squares using the program SHELXL-97.¹⁶ All H-atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the isotropic displacement parameter of the parent atom. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms. For 9.BPh₄, the crystal was mounted on a fibre and transferred to the diffractometer at *ca.* -15 °C to minimise any

possible loss of solvent. Although no solvent was located in the structure, voids of *ca.* 40 Å³ were located in the lattice. Attempts to effectively remove any electron density associated with these voids using the program Squeeze¹⁷ did not improve the model. The structure of **7**.BPh₄.2acetone contains two molecules of acetone solvent per molecule of cation. The atoms of one of the molecules of acetone are disordered over two sites, with each component assigned occupancy factors of 0.5 after trial refinement. Their geometries were restrained to ideal values. CCDC 710306 - 710309 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic data: **6**.2BPh₄: C₁₀₂H₉₈Ag₂B₂N₁₀, *M* = 1701.26, monoclinic, space group *I2/a*, *a* = 24.0034(13) Å, *b* = 17.3322(5) Å, *c* = 20.4685(7) Å, β = 104.162(4)°, *V* = 8256.7(6) Å³, *Z* = 4, *D* = 1.369 Mg m⁻³, μ = 0.531 mm⁻¹, *T*_{max/min} = 1/0.810, Crystal dimensions 0.41×0.33×0.30 mm, θ_{\max} = 34.88°, *N*_{total} = 61107, *N* = 17061, *R*_{int} = 0.0429, *N*_o = 12189, Data/restraints/parameters: 17061/0/525, *R*₁, *wR*₂ [*I*>2σ(*I*)] = 0.0377, 0.0928, *R*₁, *wR*₂ [all data] = 0.0624, 0.1006, Goodness-of-fit 0.957, Largest peak, hole (e.Å⁻³) 2.022, -0.461. **7**.BPh₄.2acetone: C₅₇H₆₁BClN₅O₂Pd, *M* = 1000.77, monoclinic, space group *P2₁/n*, *a* = 16.2612(3) Å, *b* = 14.0076(2) Å, *c* = 22.0855(8) Å, β = 99.021(3)°, *V* = 4968.4(2) Å³, *Z* = 4, *D* = 1.338 Mg m⁻³, μ = 0.475 mm⁻¹, *T*_{max/min} = 0.941/0.871, Crystal dimensions 0.432×0.357×0.142 mm, θ_{\max} = 32.79°, *N*_{total} = 66261, *N* = 17547, *R*_{int} = 0.0508, *N*_o = 12006, Data/restraints/parameters: 17547/8/642, *R*₁, *wR*₂ [*I*>2σ(*I*)] = 0.0419, 0.0905, *R*₁, *wR*₂ [all data] = 0.0724, 0.097, Goodness-of-fit 0.93, Largest peak, hole (e.Å⁻³) 1.022, -0.414.

Acknowledgement. We thank Curtin University of Technology for a Research and Teaching Fellowship (to D.H.B.).

Supporting Information Available: Synthesis and characterization details for 2,6-di(benzimidazolyl)pyridine and **5.2Br**; ^1H and ^{13}C NMR data for **6.2BPh₄** and **7.BPh₄**; compound characterization data for **8.BPh₄**; figures, refinement data and discussion of the solid-state structures of **5.2Br**, and **8.BPh₄**; additional projection of the solid-state structure of cation **6**; and cif files for **5.2Br**, **6.2BPh₄**, **7.BPh₄.2acetone** and **8.BPh₄**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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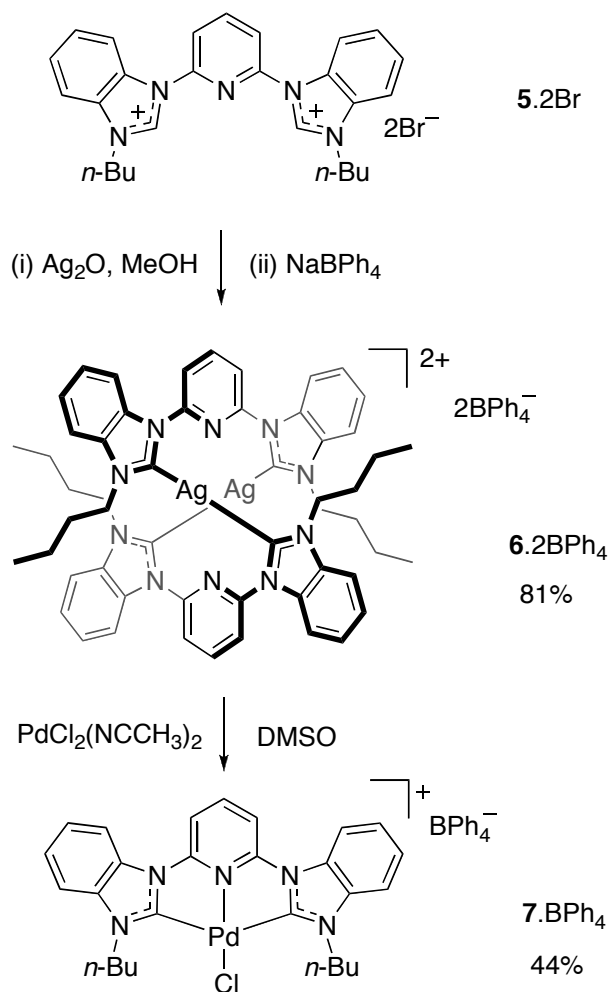
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- (15) **1.Br**: R = Bu, C-Pd-C 158.7(4)°, N-Pd-Cl 177.0(2)°; central/pendant interplanar angles 2.7(5) and 3.7(5)°; R = Me, C-Pd-C 158.5(2), N-Pd-Cl 179.0(1)°, central/pendant interplanar angles 1.6(2) and 1.4(2)°.
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Figures

Scheme 1. Synthesis of 6.2BPh₄ and 7.BPh₄



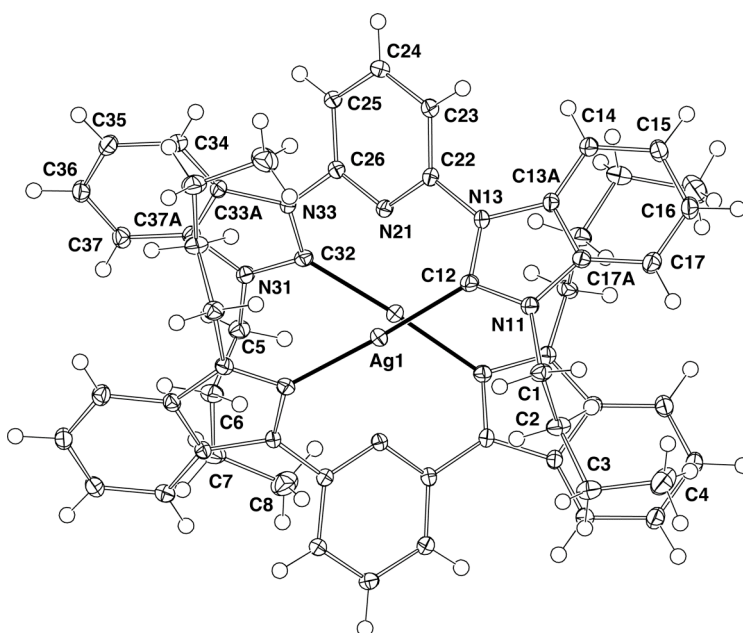


Figure 1. Molecular structure of the cation **6**, projected oblique to the Ag-Ag vector. Ellipsoids have been drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ag(1)-C(12) 2.092(1), C(12)-Ag(1)-C(32') 176.63(6) (' refers to the atom at $-x,-y,1-z$).

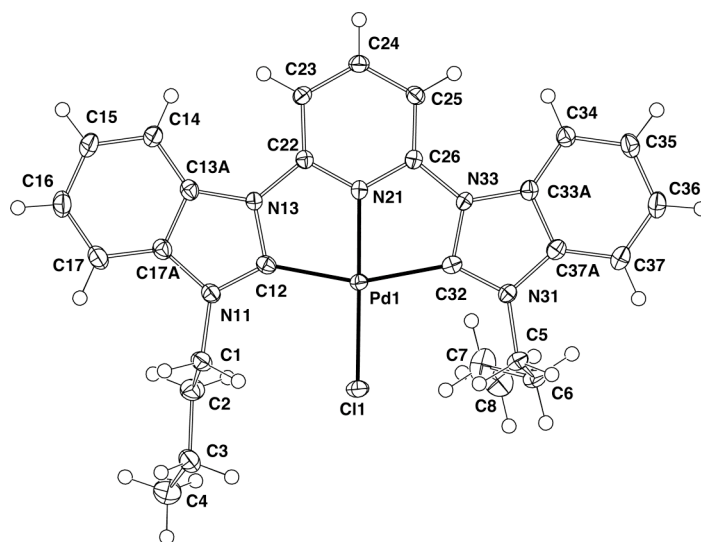
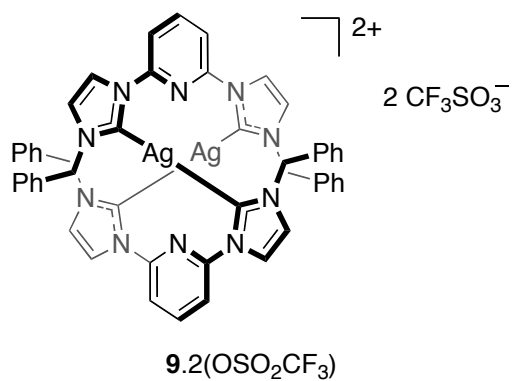
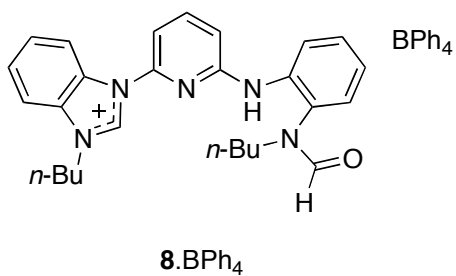
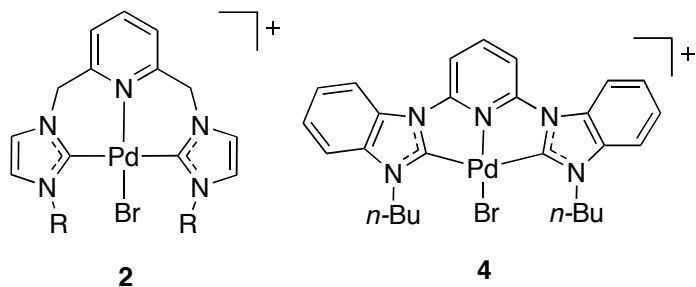
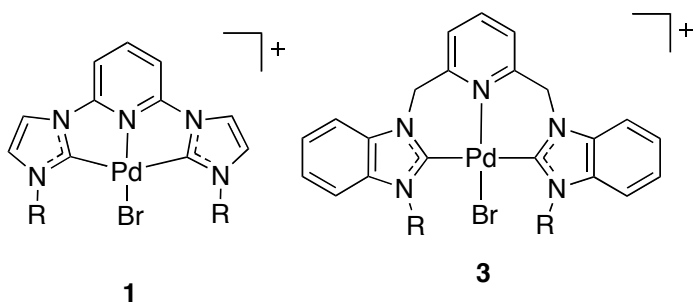


Figure 2. Molecular structure of the cation **7** projected onto the coordination plane. Ellipsoids have been drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pd(1)-N(21) 1.9701(15), Pd(1)-C(12) 2.0202(18), Pd(1)-C(32) 2.0280(18), Pd(1)-Cl(1) 2.2874(5), Pd(1)...Pd(1') 3.6105(2) (' refers to the atom at $1-x,1-y,1-z$), N(21)-Pd(1)-C(12) 79.67(7), N(21)-Pd(1)-C(32) 79.29(6), C(12)-Pd(1)-C(32) 158.94(7), N(21)-Pd(1)-Cl(1) 179.42(4), C(12)-Pd(1)-Cl(1) 99.77(5), C(32)-Pd(1)-Cl(1) 101.27(5) .



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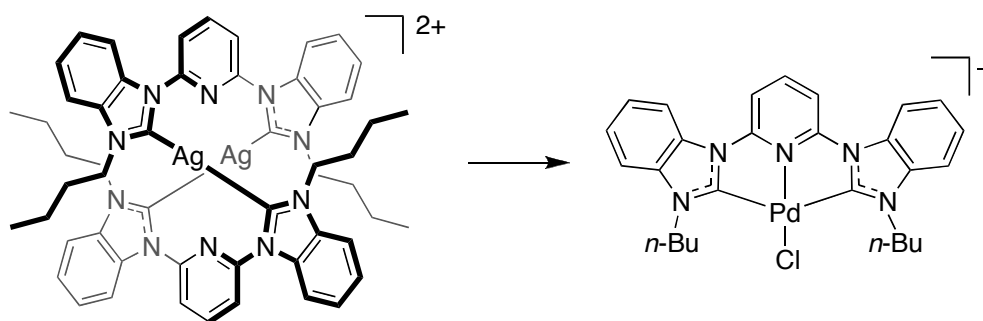
Title: **Silver and palladium complexes of a bis(benzimidazolin-2-ylidene)pyridine pincer ligand**

Authors: David H. Brown,^{*,†} Gareth L. Nealon,[†] Peter V. Simpson,[‡] Brian W. Skelton[‡] and Zhisen Wang[†]

Summary:

The synthesis and characterisation of a dinuclear silver complex bearing a bis(benzimidazolin-2-ylidene)pyridine pincer ligand is reported. Transmetalation of the ligand from silver to palladium affords a mononuclear, planar, palladium complex.

TOC graphic



Longer abstract for submission to *Chemical Abstracts*

The reaction of sodium benzimidazolate with 2,6-dichloropyridine readily affords 2,6-di(benzimidazol-1-yl)pyridine which is alkylated with 1-bromobutane to yield 2,6-bis(3-butylbenzimidazol-1-ium)pyridine dibromide. Reaction of the bis(benzimidazolium) salt with silver oxide affords a dinuclear complexes of the type $[L_2Ag_2]^{2+}$ [$L = 2,6\text{-bis(3-butylbenzimidazolin-2-ylidene)pyridine}$] with a "twisted" structure, which was identified in X-ray crystallographic studies. 1H NMR spectroscopic studies suggest that the dinuclear structure is also present in solution. Transmetalation of the silver-NHC complex with $PdCl_2(CH_3CN)_2$ yields a mononuclear palladium complex of the type $[LPdCl]^+$ [$L = 2,6\text{-bis(3-butylbenzimidazolin-2-ylidene)pyridine}$], with a chelating C,N,C -pincer ligand. The palladium complex was characterised by NMR spectroscopic and X-ray crystallographic studies. A benzimidazolium-formanilide salt was isolated from the silver oxide reaction, a product of partial hydrolysis of the bis(benzimidazolium) cation, and characterised by NMR spectroscopic and X-ray crystallographic studies.