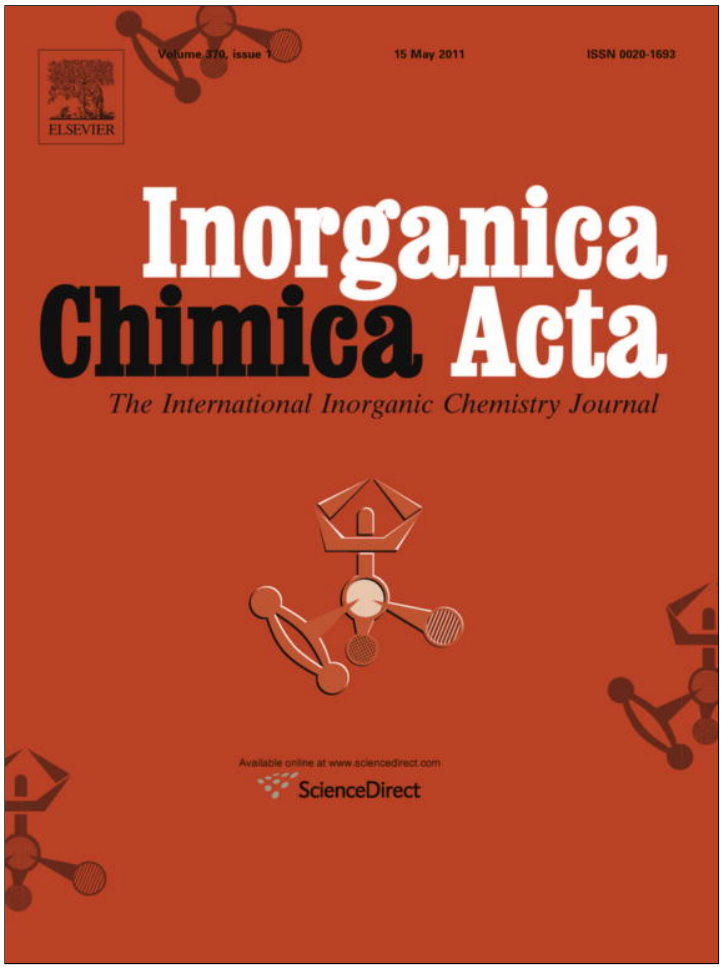

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Palladium(II) complexes of imidazolin-2-ylidene *N*-heterocyclic carbene ligands with redox-active dimethoxyphenyl or (hydro)quinonyl substituents

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ABSTRACT

Four novel imidazolium salts, precursors to *N*-heterocyclic carbene (NHC) ligands, with 2,5-dimethoxybenzyl or 2,5-dihydroxybenzyl (i.e., *p*-hydroquinone) substituents have been prepared. The crystal structure of the hydroquinone-substituted imidazolium salt $\mathbf{H_3L^3Br}$ reveals $Br^{-}\cdots H–O$ bridged chiral chains of alternating $[\mathbf{H_3L^3}]^+$ cations and Br^- counter-ions parallel to the *x*-axis. Palladium(II) complexes were accessible from reactions of the dimethoxyphenyl-substituted imidazolium precursors with palladium(II) acetate, but not from reactions of imidazolium cations with hydroquinonyl substituents. The crystal structure of the bis(dimethoxybenzyl)-substituted bis(NHC)Pd complex, *cis*-$[PdBr_2(\mathbf{L^2})]$ (**2**), is described. Puckering of the bis(NHC) ligand leads to a cleft in which an included molecule of dimethylformamide is situated. The cleft is closed by one of the dimethoxybenzyl groups which π-stacks with the dimethylformamide; the other dimethoxybenzyl group points away from the cleft and Pd(II) centre. Reaction of complex **2** with BBr_3 afforded the targeted bis(hydroquinone)-substituted bis(NHC)Pd(II) complex **3** (97% yield) which, in turn, was oxidised by 2,3-dichloro-5,6-dicyano-benzoquinone to the corresponding *p*-benzoquinone-substituted bis(NHC)Pd(II) complex **4** (98% yield). The cyclic voltammograms of the Pd(II) complexes **2–4** reveal waves that are attributed to an admix of the anticipated ligand-centred and $[Pd(C\text{-}NHC)_2Br_2]$-centred processes.

1. Introduction

Palladium(II) catalysed oxidation reactions are well known in the literature [1]. One prominent example is the Wacker process, the oxidation of ethylene to give acetaldehyde, which has been used in industry for about 50 years [2]. Other related representative examples include the oxidative addition of nucleophiles such as alcohols or amides to alkenes [3], the 1,4-oxidation of conjugated dienes [4] and the allylic oxidation of olefins [5]. Pd(II) species have also been used to catalyse the copolymerisation of alkenes and carbon monoxide to give polyketones [6], oxidation of alcohols [7], oxidative cross-coupling reactions [8], oxidative heterocyclizations [9] and even the oxidation of methane [10]. More recently, the hydroxylation of arenes under mild conditions has also been described [11].

In most of the former cases, the actual oxidants are molecular oxygen or hydrogen peroxide, which thermodynamics reveal are well able to re-oxidise the Pd(0) to Pd(II). However, the re-oxidations of Pd(0) to Pd(II) exhibit unfavourable slow kinetics. Thus an electron transfer mediator is typically added to provide satisfactorily fast catalysis (Scheme 1) [1a]. One straightforward modification of current Pd(II) complexes for oxidative catalysis would be to incorporate the redox mediator as integral part of the ligand thus enhancing electron-transfer and facilitating step B in Scheme 1.

Benzoquinone and its redox derivatives comprise perhaps the quintessential organic proton-coupled electron transfer system [12]. Benzoquinones have been used either as the final oxidant or as an electron-transfer mediator in many of the above mentioned catalytic oxidations [1,2a,2c,4–6,8,9a,10b,11]. In this paper we describe the synthesis of new Pd(II) complexes incorporating novel *N*-heterocyclic carbene (NHC) ligands adorned by electrochemically-active hydroquinonyl or quinonyl substituents positioned to facilitate direct (proton-coupled) electron transfer with the Pd centre (Scheme 2). Pd(II) complexes of *N*-heterocyclic carbene (NHC) based ligands were targeted for their high stability, ready availability and high catalytic activities [13]. Even though the use of Pd(II)-NHC complexes has been mainly restricted to C–C bond formation reactions such as Mizoroki-Heck, Suzuki-Miyaura or Buchwald-Hartwig cross-coupling processes [14], there are examples where they act as highly active and selective catalysts in oxidation reactions of the type shown in Scheme 1 [2b,7b,9c,10a,c,15].

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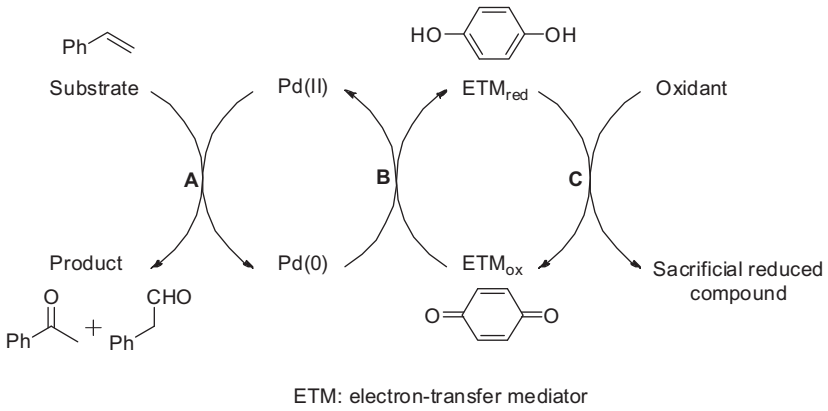
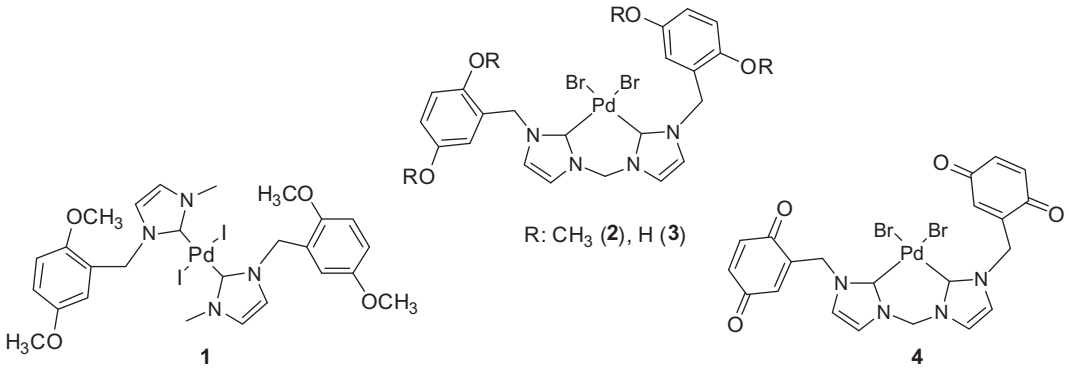


Scheme 1. Oxidation reaction catalysed by Pd(II) facilitated by an electron-transfer mediator (ETM). A Wacker-Type oxidation reaction using *p*-benzoquinone as ETM is given as an specific example.



Scheme 2. New $(NHC)_2Pd(II)$ complexes with electrochemically-active (hydro)quinonyl substituents.

2. Results and Discussion

2.1. Imidazolium salts

The synthesis of the imidazolium salt precursors **HL^{1}I** and **H$_2$L^{2}Br$_2$** required for the synthesis of complexes **1–4** is outlined in Scheme 3. The common precursor 1-(2,5-dimethoxybenzyl)-imidazole (**dbi**) was obtained by treating imidazole with NaH in DMF followed by reaction with 2,5-dimethoxybenzyl bromide. Stirring **dbi** with methyl iodide in THF afforded **HL$_1$I** in excellent overall yield. Alternatively, **dbi** was reacted with CH_2Br_2 in toluene to give **H$_2$L^{2}Br$_2$**, the precursor to a bidentate bis(NHC) ligand. Treatment of suspensions of **HL^{1}I** or **H$_2$L^{2}Br$_2$** in dichloromethane (DCM) with BBr_3, followed by methanol, yielded the hydroquinone-substituted NHC-ligand precursors **H$_3$L^{3}Br** and **H$_6$L^{4}Br$_2$**, respectively. The imidazolium salts are all easily handled and crystallised solids.

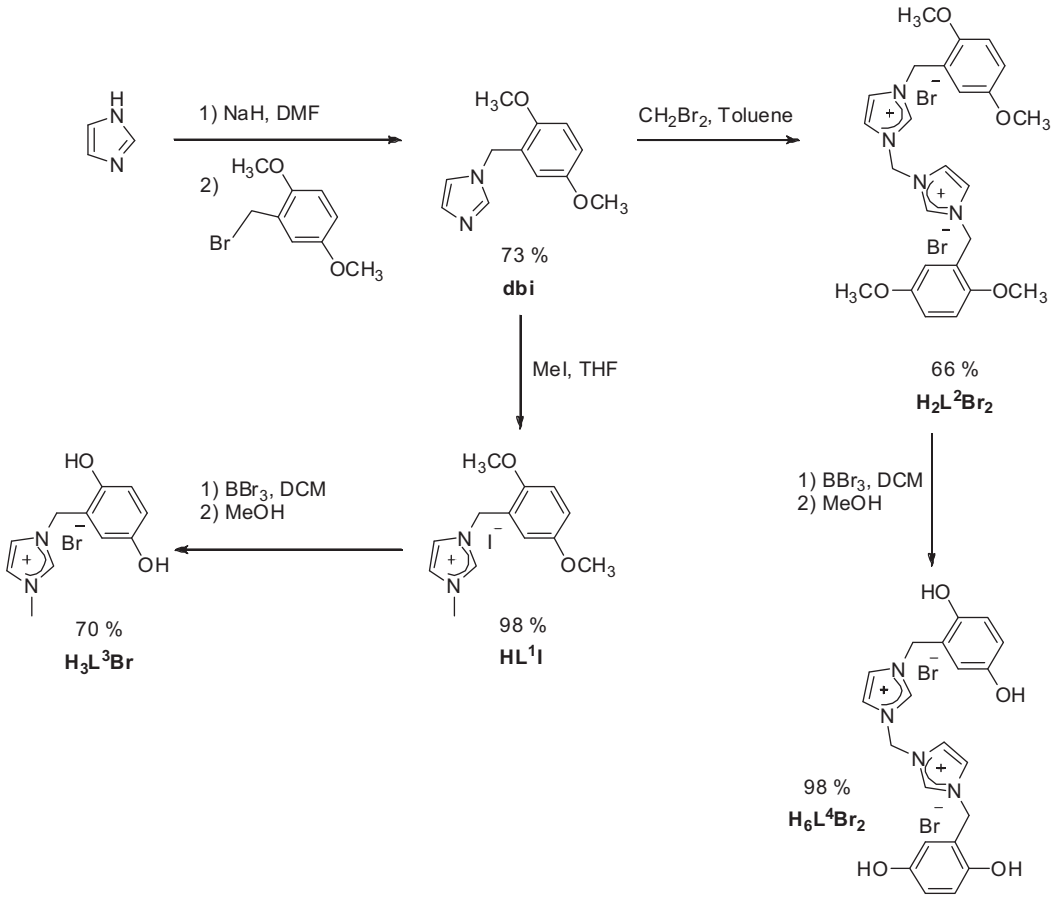
2.2. X-ray crystal structure of *H$_3$L^{3}Br*

A single crystal analysis of **H$_3$L^{3}Br** was undertaken on an apricot rod-shaped crystal grown from methanol solution. The crystal structure and labelling scheme is illustrated in Fig. 1. Significantly, atoms C1 and O1 appear ideally positioned for chelation to a metal centre. The bond angle at the benzylic bridge between the imidazolium and hydroquinonyl functional groups, N2–C5–C6, is 110.8(3)°, slightly greater than a perfect tetrahedral angle. All other bond lengths and angles are within anticipated ranges. An interesting feature is hydrogen bonding between the hydroquinone groups and the bromide ions. Each bromide ion is hydrogen bonded with two hydroxyl groups, each in an adjacent $[H_3L^3]^+$ cation; the relevant distances are O1···Br 3.172 Å and O2···Br 3.245 Å. The inter-ion hydrogen bonds lead to chiral chains parallel to the *x*-axis; each chain is paired by crystallographic inversion with one of opposite handedness that runs in the opposing direction.

2.3. Palladium(II) N-heterocyclic carbene complexes

As summarised in Scheme 4, the (dimethoxybenzyl-NHC)Pd(II) complexes $[PdI_2(L^1)_2]$ (**1**) and $[PdBr_2(L^2)]$ (**2**) were readily prepared by reaction of $Pd(OAc)_2$ with **HL^{1}I** and **H$_2$L^{2}Br$_2$**, respectively, in DMSO at 60 °C. Compound **1** was obtained as a yellow powder in a modest 20% yield. The ^{1}H NMR spectrum of **1** exhibits twice the anticipated number of peaks indicative for two species in solution. In DMSO-d_6, the relative abundance of the two species is approximately 1:1 whereas in $CDCl_3$ it is 5:2. The 5:2 mixture in $CDCl_3$ converts to a 1:1 mixture in DMSO-d_6. The results agree with simple interconversion between the *cis* and *trans* isomers of **1**, a common process in Pd(II) complexes [16].

Complex **2** was isolated as an off-white powder in 66% yield. It is surprisingly insoluble in most common lower-boiling point organic solvents. It is more readily soluble in DMF and DMSO. The ^{1}H NMR spectrum (Fig. S1, Supplementary materials) exhibits characteristic AA′ doublets at δ 6.38 and 6.32 for the non-equivalent protons of the methylene bridge (one proton points toward, and the other away, from the Pd(II) ion, see Fig. 2b vide infra), and two characteristic, but broad doublets at δ 5.70 and 5.38 for the prochiral benzylic CH_2 protons. The imidazolylidene protons appear at δ 6.74 and 7.14. The broad peaks are indicative for an



Scheme 3. Synthesis of ligand precursors HL^1I, $H_2L^2Br_2$, H_3L^3Br and $H_6L^4Br_2$.

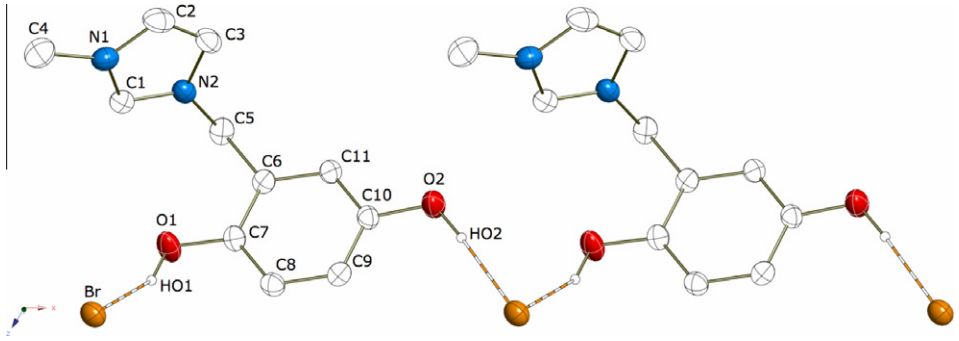
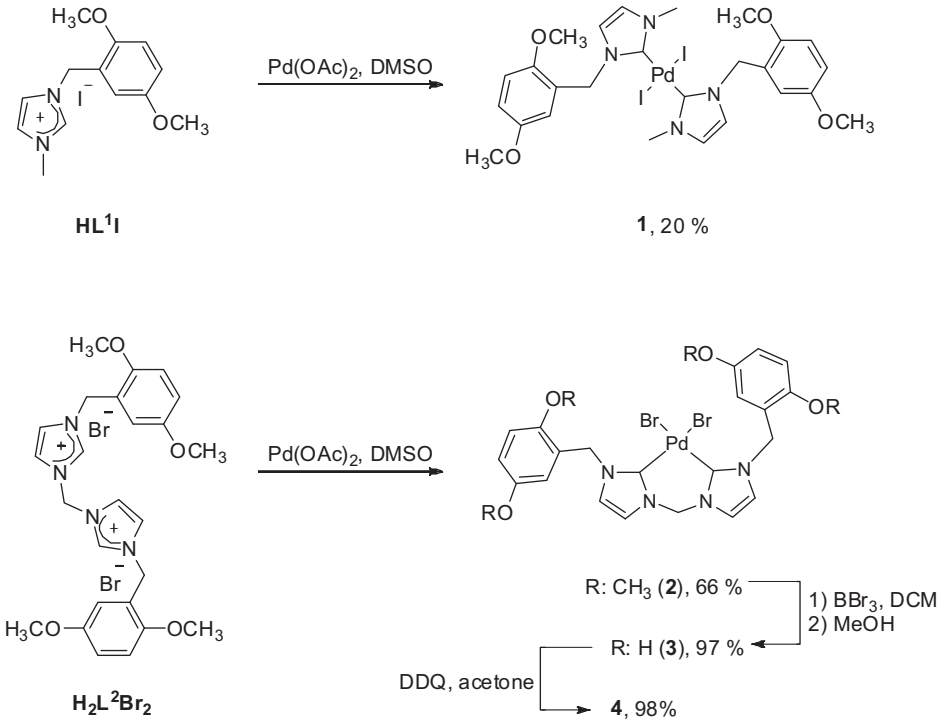


Fig. 1. View of the crystal structure for H_3L^3Br showing the labelling scheme and the H-bond interactions between the hydroquinone groups of the $[H_3L^3]^+$ cation and the bromide anions (see text); for clarity, 30% thermal ellipsoids are shown and C-bound H-atoms are deleted.

exchange process, which we believe is between the conformers of the puckered complex.

Attempts to prepare hydroquinolyl complexes by direct reaction of the imidazolium salts H_3L^3Br or $H_6L^4Br_2$ (Scheme 3) with $Pd(OAc)_2$, both with and without sodium acetate (1 equiv.) as an ancillary Brønsted base, proved unsuccessful; a palladium mirror always formed. However, the hydroquinonyl-substituted complex **3** was obtained in 97% yield by deprotection of the hydroquinonyl groups in complex **2** using BBr_3 to cleave the methoxy groups (Scheme 4). The IR spectrum of **3** reveals a new broad band at ~3350 cm^{-1} characteristic for the OH groups. The ^1H NMR spectrum of **3** shows only broad signals at 300 K. Of note, the characteristic methoxy signals of **2** are replaced by a new pair of broad signals at δ 8.55 and 8.84 corresponding to the phenolic (OH) protons. At higher temperatures, the ^1H NMR signals of **3** become sharper and better defined. In the ^1H NMR spectrum of **3** recorded at 350 K (see Fig. S2, Supplementary materials), and similarly to complex **2**, the AA′ system of the methylene bridge gives rise to two characteristic doublets at δ 6.32 and 6.41. The benzylic CH_2 protons are, in this case, magnetically equivalent and show a broad singlet at δ 5.53. Low temperature experiments were not possible due to the low solubility of the compound in suitable solvents.

To obtain the benzoquinone derivative **4**, complex **3** was treated with two equivalents of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). Complex **4** was isolated in near-quantitative yield (Scheme 4). The IR spectrum confirms the disappearance of the OH band and the growth of a strong quinone C=O peak at 1658 cm^{-1}. Interestingly, in the ^1H NMR spectrum of **4**, the bridging methylene CH_2



Scheme 4. Synthesis of complexes **1**–**4**.

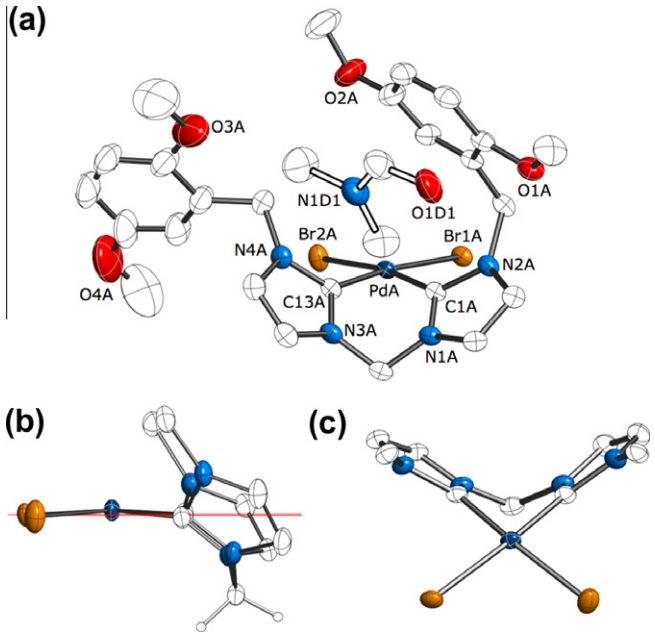


Fig. 2. (a) View showing the molecular structure and atom labelling scheme for complex **2** along with the included molecule of dimethylformamide. (b and c) Views of complex **2** with dimethoxybenzyl substituents omitted emphasising the planarity of the coordination sphere (b) and the puckering of the bis(NHC) ligand $\mathbf{L^2}$ (c). The red line in (b) is the coordination plane defined by PdA, Br1A, Br2A, C1A and C13A. For clarity, in all views 30% thermal ellipsoids are shown and H-atoms (except for the methylene bridge H-atoms in view (b)) are omitted.

protons of this compound are magnetically equivalent in contrast to complexes **2** and **3**, whereas the prochiral benzylic protons appear as two doublets at δ 5.15 and 5.80 (see Fig. S3, Supplementary materials).

2.4. X-ray crystal structure of $[PdBr_2(L^2)]$·DMF (**2**·DMF)

Recrystallisation of **2** from dimethylformamide solution under a diethyl ether atmosphere yielded **2**·DMF as clear prisms. There are two independent molecules of **2** (A and B) and two DMF in the unit cell. The independent molecules of **2** exhibit near identical geometry and bond parameters (e.g. compare Fig. 2 and Fig. S4) and so only molecule A will be discussed. The crystal structure of complex **2** is of relatively poor quality in that large thermal ellipsoids are observed for the ligand $\mathbf{L^2}$, particularly for the dimethoxybenzyl substituents, suggestive for some ligand flexibility within the crystal at 294 K, see Fig. 2a. The Pd(II) ion is bound by bis(NHC) chelate ligand $\mathbf{L^2}$ to form a puckered six-membered ring (defined by PdA, C1A, N1A, $C_{methylene}$, N3A, C13A) with a boat conformation. The PdA–C_{NHC} distances are 1.968(27) and 1.939(24) Å. Two *cisoid* bromo ligands with PdA–Br 2.503(3) and 2.470(4) Å complete the primary coordination plane of the Pd(II) ion. The maximum deviation of an atom from the coordination plane defined by PdA and the four ligand donor atoms is 0.094 Å for PdA, see Fig. 2b. The sum of the six independent X–PdA–X bond angles is 701°, which compares with 720° for a perfect square planar complex and, therefore, indicates considerable distortion within the square plane. Of most note, the C–PdA–C bite angle is 78.6(11)°. To chelate to the Pd(II) ion, the bis(NHC) ligand $\mathbf{L^2}$ has puckered, which creates a cleft that is illustrated in Fig. 2c. The angles between the carbene ring planes and the Pd coordination plane are 48.9 and 50.7°. These angles are similar to those found in related palladium(II) complexes of methylene-bridged bis-carbene ligands [16]. A molecule of dimethylformamide lies included within the cleft formed by the bis-carbene ligand. The formyl group of the dimethylformamide is π-stacked at ~3.2 Å separation with a dimethoxyphenyl group (that defined by O1A, O2A) that bends back over and caps the cleft. The other dimethoxyphenyl group of $\mathbf{L^2}$ is orientated away from the cleft and metal centre.

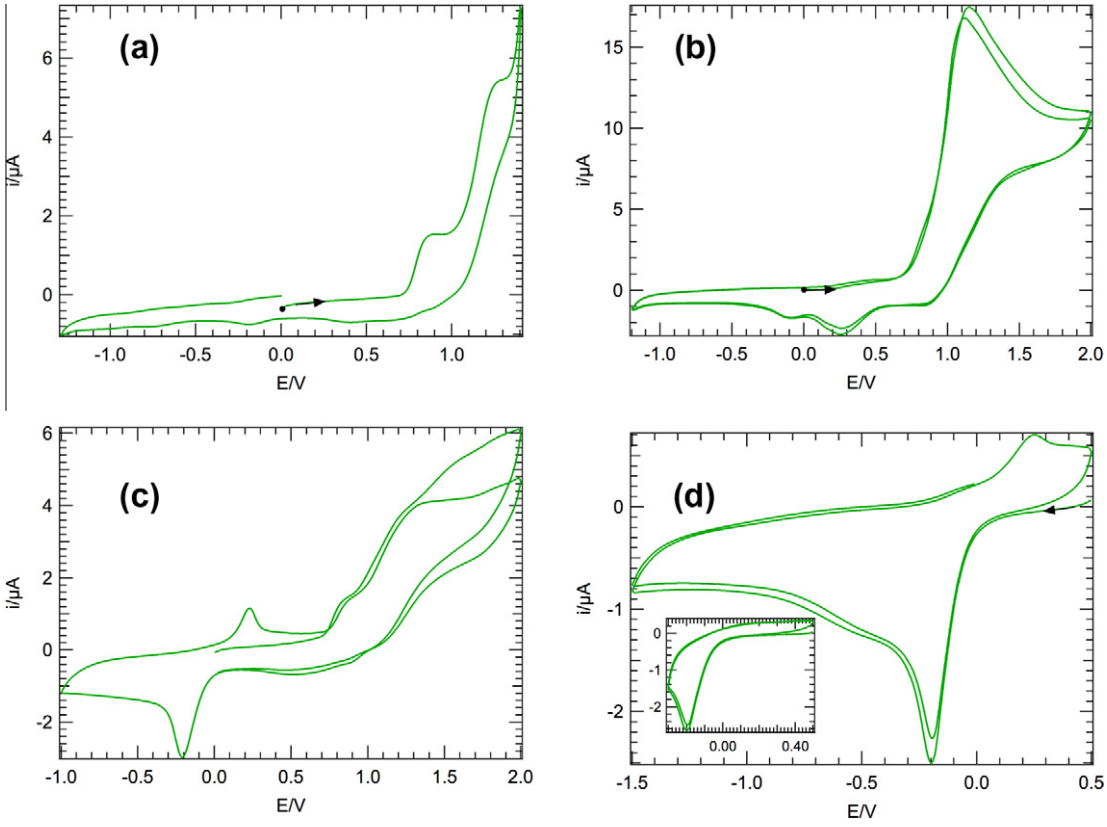


Fig. 3. Cyclic voltammograms of complexes (a) **2**, (b) **3** and (c and d) **4**. Conditions: solvent = acetonitrile – 0.1 mol L^{-1} $[NBu^n_4][PF_6]$; [complex] = 2.0 mmol L^{-1}; working electrode = freshly polished 0.5 mm diameter glassy carbon-disc; scan rate = 100 mV s^{-1}; temperature = 295 K; $E_{1/2}$ (ferrocenium-ferrocene) = 0.47 V. Note the current scales differ in (a)–(d).

2.5. Redox chemistry

The redox chemistry of complexes **2**–**4** was probed by cyclic voltammetry. Cyclic voltammograms of **2** reveal an irreversible anodic process at +0.8 V followed by a second process at *ca.* +1.2 V that exhibits double the current and some chemical reversibility (Fig. 3a). The same processes appear in the cyclic voltammograms of **3** and **4**. One possibility to be considered was that these processes originate from free bromide ion in solution derived from dissociation or substitution of the bromo ligands. However, the Br^-/Br_3^- couple appears at higher potential (at *ca.* +1.15 V [17]) than that of the first process. Thus the first process must be associated with oxidation of the $[PdBr_2(C\text{-}NHC)_2]$ centre as summarised by Eq. (1). Decomposition of $[PdBr_2(C\text{-}NHC)_2]^+$ within the electrochemical timescale (~1 ms), Eq. (2), would account for the observed irreversibility of the oxidation. The origin of the second oxidation couple cannot be definitively assigned although, based on a comparison of the anodic currents for the two consecutive oxidation processes, it must arise from two-electron oxidation of a decomposition product of the $[PdBr_2(C\text{-}NHC)_2]^+$ centre.

$$[PdBr_2(C\text{-}NHC)_2]\ (\mathbf{2}) \rightarrow [PdBr_2(C\text{-}NHC)_2]^+ + e^- \quad (1)$$

$$[PdBr_2(C\text{-}NHC)_2]^+ \rightarrow \text{decomposition product(s)} \quad (2)$$

The cyclic voltammogram of complex **3** shows the aforementioned anodic processes which overlap and merge with the characteristic anodic peak for the two-electron proton-coupled oxidation of each of the two hydroquinone substituents to give, overall, a broad peak at *ca.* 1.1 V [18] (Fig. 3b). The anodic current of the process is entirely consistent with this interpretation (for [complex] = 2.0 mM, the anodic peak current of **3** is 17 μA compared to 7 μA for **2**, i.e. ~2.4 μA/e^- or 3e^- in total for **2** and 7e^- in total for **3**). The small cathodic peak at +0.26 V in the return sweep is typical for reduction of a protonated quinone species ($[PdBr_2(C\text{-NHC-q/H}^+)_2]^{2+}$ in Eq. (3)) that is generated in the forward sweep, and is assigned as such.

$$[PdBr_2(C\text{-NHC} - hqH_2)_2]\ (\mathbf{3}) \rightleftarrows [PdBr_2(C\text{-NHC-q/H}^+)_2]^{2+} + 4e^- + 2H^+ \quad (3)$$

As already mentioned, complex **4** shares the same oxidative processes as **2** and **3** (Fig. 3c). Of more interest, however, is the reduction process at −0.2 V which is followed by a broad process at *ca.* −0.6 V. The −0.2 V process is poorly reversible and switching experiments reveal that it gives rise to a peak +0.3 V in the reverse scan. The observed cyclic voltammetry is entirely consistent with that previously observed for reactive quinones [18–21]. The first reduction corresponds to the benzoquinone-semiquinone radical anion couple, Eq. (4). The poor chemical reversibility is indicative for a reaction consuming the semiquinone anion within the electrochemical timescale (*ca.* ~1 ms). We have previously observed pendant semiquinone radical anions to bind to a metal centre, including by displacement of halogen co-ligands [19]. We have also observed internal electron transfer between semiquinone or hydroquinonyl substituents and a metal centre leading to ligand dissociation reactions [21]. Alternatively, reactive semiquinone radical anions readily abstract a proton from the solvent-electrolyte medium and may then disproportionate to afford benzoquinone and hydroquinone anion (hqH^-) [18–20]. Any of these processes would account for the poor reversibility and the diminished current for the semiquinone anion/hydroquinone dianion couple at −0.6 V (Eq. (5)). The anodic peak at +0.3 V does not occur unless the semiquinone/hydroquinone dianion couple is swept through (see Fig. 3d, inset). Thus, regardless of what the

intervening chemical step upon formation of the semiquinone radical is, the +0.3 V anodic peak must arise from oxidation of a species with coordinated or protonated hydroquinone substituent(s).

$$[PdBr_2(C\text{-NHC-q})_2]\ (\mathbf{4}) + 2e^- \rightleftarrows [PdBr_2(C\text{-NHC-sq}^{\bullet -})_2]^{2-} \quad (4)$$

$$[PdBr_2(C\text{-NHC-sq}^{\bullet -})_2]^{2-} + 2e^- \rightleftarrows [PdBr_2(C\text{-NHC-hq}^{2-})_2]^{4-} \quad (5)$$

2.6. Attempted catalysis of Wacker oxidation of styrene

Finally, preliminary assays of compounds **2**–**4** as catalysts for the Wacker oxidation of styrene were performed. Using standard reaction conditions [2c,g], no oxidation product(s) was detected after 24 h. Addition of common additives such as strong acids and/or copper co-catalysts did not improve the outcome. The presence of chloride ion may inhibit Wacker oxidation reactions [2c]. The bromo ligands in compounds **2**–**4** could similarly kill their catalytic activity.

3. Concluding remarks

A facile route to 2,5-dimethoxybenzylimidazolium and 2,5-dihydroxybenzylimidazolium (i.e., *p*-hydroquinone-substituted imidazolium) salts has been demonstrated. Pd(II) complexes of NHC ligands with dimethoxybenzyl-substituents are readily available from the 2,5-dimethoxybenzylimidazolium precursor and $Pd(OAc)_2$. The direct reaction fails for the *p*-hydroquinone-substituted imidazolium salts because the hydroquinone group reduces the palladium precursor to metallic palladium. However, Pd(II) complexes of NHC ligands with hydroquinonyl-substituents are easily obtained from the corresponding dimethoxybenzyl-substituted (NHC)Pd(II) precursors by cleavage of the methoxy groups with BBr_3. These complexes can be oxidised to afford the corresponding Pd(II) complexes of NHC ligands with quinone substituents. The crystal structure of $[PdBr_2(L^2)]\cdot$DMF (**2**·DMF) reveals the complex has a cleft capped by one of the dimethoxybenzyl substituents. In the crystal structure, the capped cleft is occupied by an included molecule of DMF. Although not explored in detail, this suggests complex **2** may behave as a small molecule receptor. Complexes **3** and **4** are expected to exhibit similar structures and, therefore, similar receptor behaviour. The redox chemistry of the $[Pd(C\text{-NHC-R})_2Br_2]$ complexes, **2**–**4**, is an admixture of consecutive oxidation processes for the Pd(II) centre and the processes characteristic for the hydroquinone or benzoquinone substituents. Unfortunately, complexes **2**–**4** do not catalyse the oxidation of styrene under Wacker conditions. Comparison with the literature for similar reactions suggests the absence of activity may be due to the bromo ligands. Finally, it is worth noting that halide-free derivatives of complexes **2**–**4** should be readily available and these may exhibit efficacious catalytic activity in oxidation reactions.

4. Experimental

4.1. General methods

Reactions were routinely performed under a dry dinitrogen atmosphere using standard Schlenk and cannula techniques. Solvents were distilled from the appropriate drying agent under dinitrogen atmosphere or taken from a Innovative Technology Pure Solvent Dispenser prior to use. NMR spectra were recorded on a Bruker DPX 300 spectrometer. Elemental analyses for C, H and N were performed in The Campbell Microanalytical Laboratory, University of Otago, New Zealand or in the Microanalytical Unit of the Research School of Chemistry, Australian National University, Canberra, Australia. The samples were dried at 40 °C for 40 h under vacuum (*ca.* 0.2 mm Hg) over phosphorus pentoxide prior to analysis. Quoted melting points are uncorrected. (+)ESI mass spectra were acquired on a VG Quattro mass spectrometer. Cyclic voltammetry measurements were performed in a conventional three electrode cell using a computer-controlled Pine Instrument Co. AFCBP1 bipotentiostat as described in detail elsewhere [19a,20a,21].

4.2. Syntheses of imidazolium salts

4.2.1. 1-(2,5-Dimethoxybenzyl)-3-methylimidazolium iodide (*HL¹I*)

Imidazole (1.90 g, 28 mmol) was dissolved in anhydrous DMF. NaH (0.74 g, 30 mmol) was added and the mixture stirred for 2 h (until the NaH had dissolved). 2,5-Dimethoxybenzylbromide [22] (4.50 g, 19 mmol) was added and the solution stirred overnight. Removal of the solvent under vacuum gave tan oil that was extracted with DCM–water mixture (20:20 mL) and the layers separated. The aqueous layer was extracted with DCM (2 × 20 mL) and then the combined organic layers were washed with brine (20 mL), dried over anhydrous magnesium sulfate and the solvent removed. The resulting yellow oil was purified by flash chromatography using a gradient elution with ethyl acetate and methanol to give 1-(2,5-dimethoxybenzyl)-3-methylimidazole (**dbi**) as a yellow oil (3.01 g, 14 mmol, 73%). δ_H ($CDCl_3$): 3.75 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 5.10 (2H, s, CH_2), 6.60 (1H, s, imidazole), 6.84 (2H, d, J = 1 Hz, Ar), 6.96 (1H, s, Ar), 7.07 (1H, s, imidazole), 7.58 (1 H, s, imidazole). *m/z* (EI-MS) 218 (M^+). A stirred solution of **dbi** (0.95 g, 4.4 mmol) and iodomethane (0.4 mL, 6.5 mmol) in THF (25 mL) was heated to 50 °C for 10 min and stirred at room temperature overnight during which time a white powder precipitated. This was collected and dried under vacuum to give compound **HL¹I** (1.5 g, 4.3 mmol, 98%). Mp: 82 °C. *Anal.* Calc. for $C_{13}H_{17}IO_2N_2$: C, 43.35; H, 4.76; N, 7.78. Found: C, 43.39; H, 4.84; N, 7.70%. δ_H ($CDCl_3$): 3.80 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 4.07 (3H, s, CH_3), 5.43 (2H, s, CH_2), 6.83 (1H, d, J = 9 Hz, Ar], 6.88 (1H, dd, J = 9 and 3 Hz, Ar], 7.28 (1H, d, J = 3 Hz, Ar], 7.37 (2H, m, imidazole), 10.05 (1H, s, imidazole). *m/z* (ESI-MS) 233 $(M-I)^+$.

4.2.2. 1,1′-Bis(2,5-dimethoxybenzyl)-3,3′-methylenediimidazolium dibromide (*H₂L²Br₂*)

The method of Gardiner et al. for preparation of a related bis(carbene) ligand was adapted here [23]. A stirred solution of **dbi** (2.70 g, 12 mmol) prepared as described above for **HL¹I** and dibromomethane (2.09 g, 12 mmol) in toluene (10 mL) was refluxed for 3 days to yield a white powder which was collected, washed with THF, recrystallised from methanol and dried under vacuum to afford **$H_2L^2Br_2$** (2.31 g, 3.8 mmol, 63%). Mp 197–198 °C. *Anal.* Calc. for $C_{25}H_{30}Br_2N_4O_4\cdot 0.5H_2O$: C, 48.48; H, 5.05; N, 9.05. Found: C, 48.10; H, 5.12; N, 9.38%. δ_H (300 MHz, $CDCl_3$): 3.74 (6H, s, OCH_3), 3.84 (6H, s, OCH_3), 5.33 (4H, s, CH_2), 6.82 (2H, d, J = 9 Hz, Ar), 6.86 (2H, dd, J = 9 and 3 Hz, Ar), 7.08 (2H, d, J = 3 Hz, Ar], 7.39 (2H, s, imidazole), 7.52 (2H, s, imidazole), 9.08 (2H, s, CH_2), 11.02 (2H, s, imidazole). *m/z* (ESI-MS) 449 $(M-2BrH)^+$.

4.2.3. 1-(2,5-Dihydroxybenzyl)-3-methylimidazolium bromide (*H₃L³Br*)

Boron tribromide (1.0 mL, 10 mmol) was added to a stirred suspension of **HL¹I** (247 mg, 0.69 mmol) in DCM (25 mL) at 0 °C. After 16 h the solution had changed from colourless to bright pink. The solvent was removed under vacuum and the resulting oil was chilled in acetone-liquid nitrogen. Methanol (*ca.* 25 mL), also chilled in acetone-liquid nitrogen, was added to the oil, the solution stirred for 15 min and then the solvent removed. The resulting apricot powder was treated with methanol (*ca.* 5 mL) and, upon cooling to −18 °C, apricot rod-shaped crystals of H_3L^3Br formed (138 mg, 0.48 mmol, 70%). Mp: 180–181 °C (decomp). *Anal.* Calc. for $C_{11}H_{13}BrN_2O_2\cdot 0.5H_2O$: C, 45.22; H, 4.83; N, 9.59. Found: C,

45.34; H, 4.68; N, 9.35%. δ_H (DMSO-d_6) 3.82 (3H, s, CH_3), 5.19 (2H, s, CH_2), 6.61 (1H, dd, J = 3 and 9 Hz, Ar), 6.66 (1H, d, J = 3 Hz, Ar), 6.69 (1H, d, J = 9 Hz, Ar), 7.66 (2H, s, imidazole), 8.90 (1H, s, OH), 9.08 (1H, s, OH), 9.33 (1H, s, imidazole). *m/z* (ESI-MS) 205 $(M-Br)^+$.

4.2.4. 1,1′-Bis(2,5-dihydroxybenzyl)-3,3′-methylenediimidazolium dibromide (***$H_6L^4Br_2$***)

Boron tribromide (0.6 mL, 6 mmol) was added to a stirred solution of **$H_2L^2Br_2$** (0.12 g, 0.20 mmol), in DCM (20 mL) at 0 °C. A white precipitate formed immediately. After 16 h the solvent was removed under vacuum and the resulting oily residue was dissolved in methanol (*ca.* 20 mL), which had been chilled in acetone-liquid nitrogen. The methanol was removed to yield a white solid, **$H_6L^4Br_2$** (109 mg, 0.19 mmol, 98%). Mp: 242 °C (decomp). *Anal.* Calc. for $C_{21}H_{22}Br_2N_4O_4{\cdot}H_2O$: C, 44.38; H, 4.25; N, 9.86. Found: C, 43.63; H, 4.13; N, 9.51%. δ_H (DMSO-d_6) 5.23 (4H, s, CH_2), 6.59 (2H, s, CH_2), 6.64 (2H, dd, J = 3 and 9 Hz, Ar), 6.72 (2H, d, J = 9 Hz, Ar), 6.73 (2H, d, J = 3 Hz, Ar), 7.79 (2H, s, imidazole), 7.97 (2H, s, imidazole), 8.96 (2H, s, OH), 9.39 (2H, s, imidazole), 9.41 (2H, s, OH). *m/z* (ESI-MS) 473 $(M-Br)^+$.

4.3. Syntheses of (NHC)Pd(II) complexes

4.3.1. Bis[1-(2,5-dimethoxybenzyl)-3-methylimidazolin-2-ylidene]-diiodopalladium(II) (***1***)

A stirred DMSO solution (3 mL) of $Pd(OAc)_2$ (51 mg, 0.22 mmol) and **HL^1I** (158 mg, 0.46 mmol) was heated to 60 °C for 24 h. The solvent was removed under vacuum and the residue extracted with MeCN. After chilling the solution to −18 °C yellowish solid precipitated, which was collected, washed with diethyl ether and air-dried (35 mg, 0.04 mmol, 20%). Mp: 222–224 °C. *Anal.* Calc. for $C_{26}H_{32}I_2N_4O_4Pd$: C, 37.86; H, 3.91; N, 6.79. Found: C, 37.85; H, 4.07; N, 6.62%. δ_H (DMSO-d_6) shows *cis* and *trans* isomers: 3.55, 3.63, 3.67, 3.80 (6H, s, OCH_3), 3.75, 3.83 (6H, s, CH_3), 5.36 (2H, s, CH_2), 5.45 (2H, s, CH_2), 6.75–6.88 (6H, m, Ar), 7.04 (2H, m, imid), 7.28 (2H, m, imid). δ_C (75 MHz, dmso-d_6) shows *cis* and *trans* isomers; 32.21, 32.30 (CH_3), 48.44, 48.59 (CH_2), 55.72, 55.79, 56.02, 56.19 (OCH_3), 112.02, 112.14, 114.40, 114.46, 115.76, 116.01 (Ar), 150.93, 151.08, 153.29, 153.34 (imidazole).

4.3.2. [1,1′-Bis(2,5-dimethoxybenzyl)-3,3′-methylenediimidazolin-2,2′-diylidene] dibromo palladium(II) (***2***)

A stirred DMSO solution (3 mL) of $Pd(OAc)_2$ (51 mg, 0.22 mmol) and **$H_2L^2Br_2$** (136 mg, 0.22 mmol) was heated to 60 °C for 24 h. The solvent was removed under vacuum and the residue extracted into MeCN, from which, after vigorous mixing, an off-white powder precipitated. Diethyl ether was added and the solid collected, washed with diethyl ether and air-dried. The product was dissolved in DMF, the solution filtered through cellite, and then crystallised by diffusion of diethyl ether vapour to give clear prisms of **2** (103 mg, 0.14 mmol, 66%). Mp: 287–290 °C (decomp). *Anal.* Calc. for $C_{25}H_{30}Br_2N_4O_4Pd{\cdot}0.5dmf$: C, 42.54; H, 4.24; N, 8.43. Found: C, 42.47; H, 4.29; N, 8.43%. δ_H (DMSO-d_6) 3.60 (6H, s, OCH_3), 3.72 (6H, s, OCH_3), 5.38 (2H, d, J = 14.2 Hz, CH_AH_B), 5.71 (2H, d, J = 14.2 Hz, CH_AH_B), 6.32 (1H, d, J = 13.2 Hz, CH_AH_B), 6.38 (1H, d, J = 13.2 Hz, CH_AH_B), 6.74 (2H, s, imidazole), 6.81 (2H, d, J = 9 Hz, Ar), 6.91 (2H, d, J = 9 Hz, Ar), 7.14 (2H, s, imidazole), 7.59 (2H, s, Ar). *m/z* (ESI-MS) 634 $(M-Br)^+$.

4.3.3. 1,1′-Bis(2,5-dihydroxybenzyl)-3,3′-methylenediimidazolin-2,2′-diylidene]di-bromopalladium(II) (***3***)

Boron tribromide (0.9 mL, 9.5 mmol) was added dropwise to a stirred solution of **2** (260 mg, 0.36 mmol) in DCM (20 mL) previously cooled in an acetone-liquid nitrogen slush bath (−80 °C). The mixture was kept at this temperature for one hour and then allow to warm up to room temperature and stirred overnight. The mixture was cooled down again into an acetone-liquid nitrogen slush bath and 30 mL of methanol were added slowly. The solvent was then removed under vacuum to give a brown-orange solid, which was recrystallised from methanol to yield a white solid (230 mg, 0.35 mmol, 97%). Mp: 265–267 °C (decomp). *Anal.* Calc. for $C_{21}H_{20}Br_2N_4O_4Pd$: C, 38.33; H, 3.06; N, 8.52. Found: C, 38.24; H, 3.00; N, 8.40%. δ_H (T = 350 K, DMSO-d_6) 5.53 (4H, s, CH_2), 6.32 (1H, d, J = 12.7 Hz, CH_AH_B), 6.41 (1H, d, J = 12.7 Hz, CH_AH_B), 6.63 (2H, dd, J = 2.5 and 8.7 Hz, Ar), 6.74 (2H, d, J = 8.7 Hz, Ar), 6.80 (1H, s, imidazole), 7.06 (2H, s, imidazole), 7.57 (2H, J = 2.5 Hz, Ar), 8.55 (2H, s broad, OH), 8.84 (2H, s broad, OH). *m/z* (ESI-MS) 578 $(M-Br)^+$.

4.3.4. [1,1′-Bis(toluquinonyl)-3,3′-methylenediimidazolin-2,2′-diylidene]dibromo palladium(II) (***4***)

A solution of DDQ (27 mg, 0.12 mmol) in acetone (2 mL) was added to a solution of **3** (40 mg, 0.06 mmol) in acetone (10 mL). The resulting solution was stirred for 30 min during which time a pale yellow precipitate formed. The precipitate was collected, washed with acetone and air-dried to give **4** as a pale yellow solid (39 mg, 0.059 mmol, 98%). Mp: 218–220 °C (decomp). *Anal.* Calc. for $C_{21}H_{16}Br_2N_4O_4Pd$: C, 38.52; H, 2.46; N, 8.54. Found: C, 38.72; H, 2.59; N, 8.36%. δ_H (DMSO-d_6) 5.15 (2H, d, J = 18.0 Hz, CH_AH_B), 5.80 (2H, d, J = 18.0 Hz, CH_AH_B), 6.12 (2H, s broad, CH_2), 6.37 (2H, s, Ar), 6.81–6.90 (4H, m, Ar), 7.38 (2H, d, J = 3 MHz, imidazole), 7.68 (2H, d, J = 3 MHz, imidazole). *m/z* (ESI-MS) 654 (M^+). ν_{max}/cm^{-1} (CO) 1657s (KBr disc).

4.4. General procedure for Wacker oxidation reactions

The Pd(II) complex **2**, **3** or **4** (0.01 mmol) was dissolved in a mixture of DMF/water (3:1, 1.0 mL) under air. Styrene (0.5 mmol) was added and the mixture stirred at 60 °C. Reaction progress was monitored by GC–MS.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.02.007.

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