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# Synthesis and structure of $C_2$-symmetric *N*-heterocyclic carbene complexes of palladium

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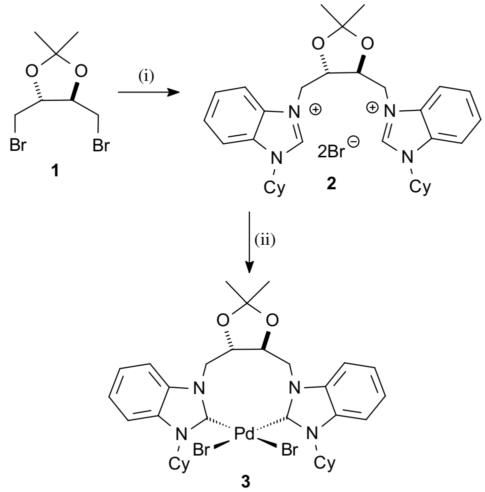
**Abstract**—The first 9- and 11-membered *cis* and *trans* $C_2$-symmetric benzimidazol-2-ylidene palladium(II) complexes based on a *trans*-2,2-dimethyl-1,3-dioxalane backbone were synthesised and the configuration of the complexes was elucidated via NMR and X-ray crystallography.

In recent years, synthetic efforts towards transition metal complexes containing *N*-heterocyclic carbene ligands (NHC) have been the subject of intense interest.[1–3] Major stimuli for the renewed appeal of these complexes lie in their use as catalysts, where they often display significant advantages over the analogous phosphine-containing compounds.[4–6] In catalytic systems, NHCs have been shown to prevent the formation of elemental metal, a problem often associated with weak ligand–metal interactions.[7] Consequent stability towards heat, oxygen and moisture has led to palladium, rhodium and ruthenium complexes of NHCs featuring prominently in catalytic reactions for which these metals are already well known.[4–6,8–11]

The literature abounds with examples of chiral monodentate carbene complexes designed for asymmetric synthesis,[12–14] but, until recently, $C_2$-symmetric bidentate complexes were notable by their absence. Although a Heck active 11-membered chelated chiral NHC palladium complex was prepared by RajanBabu and co-workers a mixture of both *cis*- and *trans*-square planar geometries was obtained.[15] Mindful of this, we began the synthesis of $C_2$-symmetric complexes containing a *trans*-2,2-dimethyl-1,3-dioxalane backbone of varying chelate size in an attempt to prepare exclusive *cis* or *trans* geometries.

Manipulation of commercially available enantiopure tartaric acid by conventional means[16,17] gave access to 4,5-*bis*(bromomethyl)-2,2-dimethyl-1,3-dioxolane **1**, which when heated with 1-cyclohexylbenzimidazole produced an almost quantitative yield of the salt **2** as a glassy solid. The crude diazolium salt was reacted under a temperature gradient with palladium acetate in DMSO according to Herrmann and Schwarz[18] to yield the chelate **3**. The complex was obtained in a yield of 61% and fully characterised by NMR spectroscopy, HRMS and X-ray crystallography (Scheme 1).



**Scheme 1.** Synthesis of *cis* dicarbene palladium(II) complex **3**. Reagents and conditions: (i) 1-cyclohexylbenzimidazole, 99%; (ii) $Pd(OAc)_2$, DMSO, 61%.

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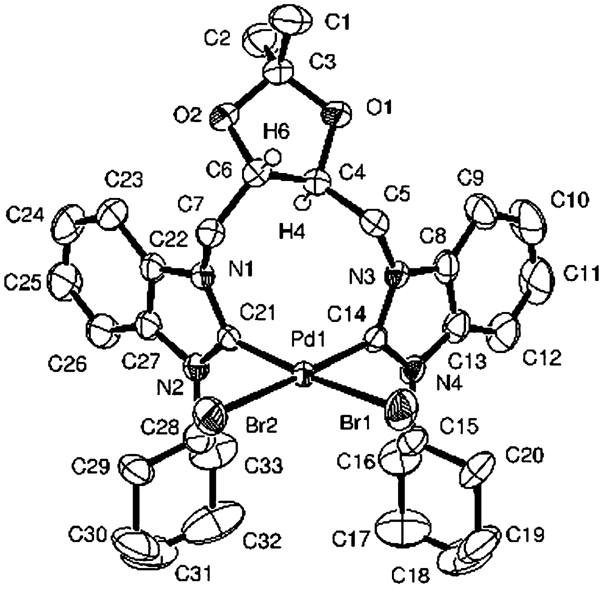
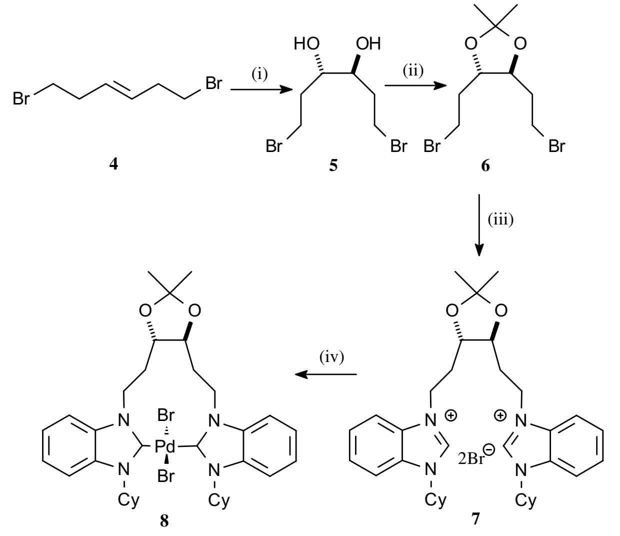


**Figure 1.** ORTEP diagram of **3** (50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): Pd1–C14 = 1.996 (3), Pd1–C21 = 1.997 (3), Pd1–Br1 = 2.4731 (4), Pd1–Br2 = 2.4734 (4), C14–Pd1–C21 = 95.16 (12), Br1–Pd1–Br2 = 94.279 (18), C14–Pd1–Br1 = 84.98 (9), C21–Pd1–Br2 = 85.26 (9), C21–Pd1–Br1 = 173.71 (9), C14–Pd1–Br2 = 177.09 (10), N2–C21–N1 = 106.9 (3), N4–C14–N3 = 106.2 (3).

The absence of the signal for the $N_2CH$ proton in the $^1H$ NMR spectrum indicated the complexation was successful. The $^{13}C$ NMR spectrum revealed a complex structure in solution. Resonances of the ylidene carbon atoms co-ordinated to the palladium centre were seen at 173.5 and 174.9 ppm, indicating a slightly different environment for each. By comparisons with spectroscopic data of literature examples of benzimidazol-2-ylidene palladium complexes it appeared clear that **3** had a *cis* configuration.[19] By evaporation of a dichloromethane solution, crystals of **3** suitable for X-ray structural analysis were obtained as the toluene solvate, which was present from the reaction work-up. The configuration of the complex was confirmed by X-ray crystallography (Fig. 1).

The structure determination of the solid complex revealed a near perfect square planar geometry about palladium (sum of angles around palladium 359.7°). The bond lengths (1.996 Å) of the ylidene carbon palladium bonds are similar to those in known *cis* complexes.[19] The bond angles, C–Pd–C and Br–Pd–Br, both ~95°, are larger than corresponding methylene bridged bis-carbene complexes. These existing complexes contain iodide counterions and the size difference between iodide and bromide may be reflected in the bond angles at palladium. The dioxolane backbone may also influence the bond angles around the palladium. It appears the size of the ligand allows only one configuration of the chelate as there was no spectroscopic or crystallographic evidence for the *trans* geometry. As NHC palladium(II) complexes are known to be Heck active, it is anticipated the chiral chelate **3** will allow stereodifferentiating Heck coupling reactions.



**Scheme 2.** Synthesis of *trans* dicarbene palladium(II) complex **8**. Reagents and conditions: (i) $(DHQ)_2PHAL$, $K_2OsO_2(OH)_4$, $K_3Fe(CN)_6$, $H_2O$, $Bu^tOH$, $MeSO_2NH_2$, $NaHCO_3$, $K_2CO_3$, 67%; (ii) $(CH_3)_2O(CH_3)_2$, PhMe, TsOH, 95%; 1-cyclohexylbenzimidazole, 99%; $Pd(OAc)_2$, DMSO, 88%.

Attention was then turned to the preparation of an 11-membered complex; by increasing the chain length of the bridge the flexibility of the ligand would improve, and therefore affect the potential chelate bite angle. Commercially available β-hydromuconic acid was converted to *trans*-1,6-dibromohex-3-ene **4** by conventional methods.[16,17,20] Employing Sharpless asymmetric dihydroxylation[21] the chiral diol **5** was obtained in a yield of 67%. The optical rotation, $[\alpha]_D^{28}$ −59.2 (*c* 2.2, $CHCl_3$), is in agreement with Cope and Shen[22] who prepared the same molecule from enantiopure mannitol. Employing the same procedures as with **3** the *trans* chelate **8** was obtained in a yield of 88% from the diazolium salt **7**. The yellow complex was characterised by NMR spectroscopy, HRMS and X-ray crystallography (Scheme 2).

The methylenes connected to the heterocyclic ring in the complex have diastereotopic geminal protons resonating at 4.54 and 5.26 ppm as two complex hydrogen multiplets. The $^{13}C$ NMR spectrum revealed the complex was $C_2$-symmetric in solution with single peaks for the backbone representing two carbons similar to the salt precursor. The Pd–C resonance was found at 181, ~7 ppm downfield compared to the corresponding peaks for the *cis* complex of **3**. These observations indicated that the 11-membered complex was a *trans* chelate exclusively due to the absence of peaks around 173 ppm, which would be present for a mixture of *cis* and *trans* geometries. This was confirmed by X-ray crystallography. Crystals of the chelate suitable for X-ray structural analysis were obtained by careful layering of diethyl ether onto a tetrahydrofuran solution of **8** (Fig. 2). The palladium has a distorted square planar arrangement, with a chelating bite angle of 175.4° and a Br–Pd–Br angle 177.23°. Pd–C bond lengths are ~0.03 Å longer than those of the corresponding *cis* complex. This indicates that the *trans* 11-membered chelate has resulted in a less congested environment at the palla-

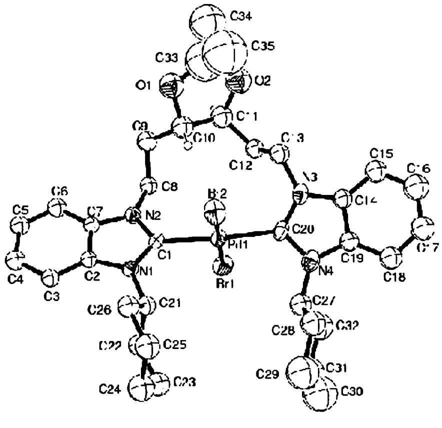


**Figure 2.** ORTEP diagram of **8** (40% displacement ellipsoids). Selected bond lengths (Å) and angles (°): Pd1–C1 = 2.024 (9), Pd1–C20 = 2.029 (10), Pd1–Br1 = 2.4410 (13), Pd1–Br2 = 2.4446 (13), C1–Pd1–C20 = 175.4 (4), Br1–Pd1–Br2 = 177.23 (6), C1–Pd1–Br1 = 90.1 (3), C1–Pd1–Br2 = 90.3 (3), C20–Pd1–Br1 = 90.8 (3), C20–Pd1–Br2 = 89.0 (3), N2–C1–N1 = 107.4 (7), N4–C20–N3 = 108.2 (8).

dium centre than the nine-membered *cis* system. In view of this, the *cis* chelate may induce stereoselectivity to a higher degree.

In conclusion, the synthesis of the first chiral nine-membered NHC palladium chelate was achieved by the elaboration of tartaric acid to a bis(benzimidazolium) salt, which was deprotonated in situ with palladium acetate to afford the *cis* configuration of the complex, exclusively. Increasing the chain length and flexibility of the backbone by two methylene groups gave solely the *trans* configuration of the palladium complex. This compound was prepared using asymmetric dihydroxylation across *trans*-1,6-dibromohex-3-ene. The configuration of the complexes was elucidated via NMR spectroscopy and confirmed by X-ray crystallography.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 225624 and 225625. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

*Preparation and spectroscopic data of* **3**: A mixture of (4*S*,5*S*)-4,5-bis(1-cyclohexylbenzimidazolium-3-methyl)-2,2-dimethyl-1,3-dioxolane dibromide (250 mg, 0.36 mmol), palladium acetate (82 mg, 0.36 mmol) and dimethyl sulfoxide (8 cm$^3$) was heated to 50 °C for 4 h, after which the temperature was increased to 150 °C and the mixture stirred for 30 min. Distillation of the dimethyl sulfoxide under reduced pressure gave a yellow residue, which was extracted with toluene (3 × 5 cm$^3$). The toluene extracts were concentrated under reduced pressure to yield the *bidentate carbene palladium complex* (175 mg, 61%) as a yellow solid; mp 238 °C; $[\alpha]_D^{23}$ −20.6 (*c* 0.85, $CH_2Cl_2$); $\nu_{max}$ (KBr)/cm$^{-1}$ 2931 (s), 2856 (m), 1616 (m), 1477 (s), 1446 (m), 1398 (s), 1373 (s), 1344 (m), 1232 (m), 1093 (s), 1045 (w), 744 (s); $\delta_C$ (62.9 MHz; $CDCl_3$) 25.2 ($CH_2$), 25.4 ($CH_2$), 25.5 ($CH_2$), 25.6 ($CH_2$), 26.3 ($CH_2$), 26.6 ($CH_2$), 27.0 ($O_2C(CH_3)_2$), 27.4 ($CH_2$), 30.3 ($CH_2$), 30.4 ($CH_2$), 31.0 ($CH_2$), 46.7 ($NCH_2$), 46.9 ($NCH_2$), 62.0 (N*C*H), 63.0 (N*C*H), 77.3 (O*C*H), 79.2 (O*C*H), 110.6 ($O_2C(CH_3)_2$), 113.0 (Ar*C*H), 113.1 (Ar*C*H), 113.2 (Ar*C*H), 113.3 (Ar*C*H), 122.9 (Ar*C*H), 123.1 (Ar*C*H), 123.3 (Ar*C*H), 123.6 (Ar*C*H), 132.5 (N*C*), 132.6 (N*C*), 135.5 (N*C*), 137.0 (N*C*), 173.5 ($N_2CPd$), 174.9 ($N_2CPd$). *m/z* (LSIMS), 815.2 (10%, $[M+Na]^+$), 711.2 (100%, $[M-Br]^+$), 631.2 (23%, $[M-2Br]^+$), (EI) 711.1533 ($[M-Br^{(79)}]^+$, $C_{33}H_{42}N_4O_2Pd^{(106)}Br^{(79)}$ requires 711.1526).

*Spectroscopic data* of **8**: Mp 276 °C; $[\alpha]_D^{23}$ −88.8 (*c* 1.2, $CH_2Cl_2$); $\delta_H$ (250 MHz; $CDCl_3$) 1.43 (6H, s, $O_2C(CH_3)_2$), 1.54–2.50 (20H, m, C*H*$_2$), 2.83 (2H, m, C*H*$_2$), 3.11–3.08 (2H, m, C*H*), 4.51–4.54 (2H, dd, *J* 8.0 and 7.0, NC*H*$_2$), 4.74 (2H, br s, OC*H*), 5.23–5.29 (2H, dd, *J* 7.5 and 7.3, NC*H*$_2$), 5.58 (2H, m, NC*H*), 7.20–7.25 (4H, m, Ar*H*), 7.37–7.41 (2H, m, Ar*H*), 7.57–7.61 (2H, m, Ar*H*); $\delta_C$ (62.9 MHz; $CDCl_3$) 25.6 ($CH_2$), 26.3 ($CH_2$), 26.4 ($CH_2$), 27.2 ($O_2C(CH_3)_2$), 31.2 ($CH_2$), 31.4 ($CH_2$), 31.6 ($CH_2$), 43.9 ($NCH_2$), 62.7 (N*C*H), 78.1 (O*C*H), 108.1 ($O_2C(CH_3)_2$), 110.2 (*C*H), 112.8 (*C*H), 122.4 (*C*H), 122.8 (*C*H), 132.8 (N*C*), 136.0 (N*C*), 180.9 ($N_2CPd$); *m/z* (EI) 739.1844 ($[M-Br^{79}]^+$, $C_{35}H_{46}N_4O_2Pd^{(106)}Br$ requires 739.1839), (LSIMS), 741.3 (100%, $[M-Br]^+$), 821.3 (55%, $[M+H]^+$).

*Crystal data for* **3**: Empirical formula $C_{40}H_{50}Br_2N_4O_2Pd$ (including a solvated toluene molecule), formula weight 885.06, temperature 298 (2) K, wavelength 0.71073 Å, monoclinic, space group $P_1$ unit cell dimensions $a = 11.2377$ (4) Å, $b = 9.4658$ (3) Å, $c = 17.9815$ (6) Å, $\beta = 92.242$ (1)°, $V = 1911.30$ (11) Å, $Z = 2$, $D_c = 1.538$ Mg m$^{-3}$, absorption coefficient 2.615 mm$^{-1}$, $F(000) = 900$, crystal size 0.38 × 0.18 × 0.10 mm, theta range for data collection 1.13–27.50°, index ranges $-14 \leqslant h \leqslant 14$, $-12 \leqslant k \leqslant 12$, $-19 \leqslant l \leqslant 23$, reflections collected 13,394, independent reflections 8182 [$R_{int} = 0.023$], completeness to $\theta = 27.50°$, 99.7%, max. and min. transmission = 0.780 and 0.437, refinement method full-matrix least-squares on $F^2$ data/restraints/parameters 8182/1/407, goodness-of-fit on $F^2 = 1.007$, final *R* indices [$I > 2\sigma(I)$], $R1 = 0.029$, $wR2 = 0.070$, *R* indices (all data), $R1 = 0.034$, $wR2 = 0.071$, absolute structure parameter 0.028 (6), largest diff. peak and hole 0.54 and −0.39 e Å$^{-3}$.

*Crystal data for* **8**: Empirical formula $C_{35}H_{46}Br_2N_4O_2Pd$, formula weight 820.98, temperature 293 (2) K, wavelength 0.71073 Å, monoclinic, space group $P2_1/n$, unit cell dimensions $a = 16.9261$ (10) Å, $b = 13.0734$ (8) Å, $c = 16.7012$ (10) Å, $\beta = 96.053$ (1)°, $V = 3675.1$ (4) Å$^3$, $Z = 4$, $D_c = 1.484$ Mg m$^{-3}$, absorption coefficient = 2.714 mm$^{-1}$, $F(000) = 1664$, crystal size 0.20 × 0.16 × 0.13 mm, theta range for data collection 1.6325.16°, index ranges $-20 \leqslant h \leqslant 18$, $-15 \leqslant k \leqslant 15$, $-19 \leqslant l \leqslant 19$, reflections collected 21,555, independent reflections 6513 [$R_{int} = 0.110$], completeness to $\theta = 25.16°$ 99.0%, refinement method full-matrix least-squares on $F^2$ data/restraints/parameters 6513/0/

207, goodness-of-fit on $F^2$ 1.018, final $R$ indices $[I > 2\sigma(I)]$ $R1 = 0.075$, $wR2 = 0.195$, $R$ indices (all data) $R1 = 0.144$, $wR2 = 0.230$, largest diff. peak and hole 1.51 and 1.20 e Å$^{-3}$.

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