Supplementary Material (ESI) for Dalton Transactions

Steric control over the formation of *cis* and *trans* bischelated palladium(II) complexes using a new series of flexible *N,P* pyridyl-phosphine ligands

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Supporting Information — X-Ray Crystallography

Solid State Intermolecular Aspects of the Structures

*Compound **7a*** - The molecules pack to form centrosymmetric dimer pairs, one of the C(1) methylene protons in one molecule approaching the centroid of the N(4) pyridyl ring in its C_i-related counterpart with H···π 2.95 Å and C–H···π 121°, the H···π vector being inclined by *ca.* 77° to the ring plane.

*Compound **10*** - Centrosymmetrically related pairs of molecules are linked by a π-π stacking interaction between pyridyl rings with centroid···centroid and mean interplanar separations of *ca.* 3.77 and 3.54 Å respectively (the two rings are perfectly parallel as a consequence of the centre of symmetry). The other face of the pyridyl ring is approached by a cyclohexyl methylene proton with H···π 3.52 Å and C–H···π 170° (the H···π vector being inclined by *ca.* 53° to the ring plane), though this contact is somewhat long. These two interactions subtend an angle of *ca.* 160° at the pyridyl ring centroid.

*Compound **11*** - Adjacent centrosymmetrically related molecules are again linked by a π-π stacking interaction between pyridyl rings, the centroid···centroid and mean interplanar separations being *ca.* 3.85 and 3.37 Å respectively. The opposite face of the ring is approached by a *t*-butyl proton with H···π 3.07 Å and C–H···π 131°, the H···π vector being inclined by *ca.* 70° to the ring plane, and these two interactions subtend an angle of *ca.* 144° at the pyridyl ring centroid.

*Compound **12*** – There is a short intermolecular C–H···π approach to the pyridyl ring from a methyl proton on C(9) of an adjacent molecule [H···π 2.75 Å and C–H···π 158°, the H···π vector being inclined by *ca.* 82° to the ring plane]. There are no strong contacts to the other side of the pyridyl ring, the closest approaches being from cyclohexyl methylene [H···π 3.81 Å and C–H···π 140°, the H···π vector being inclined by *ca.* 45° to the ring plane] and pyridyl C–H [H···π 3.90 Å and C–H···π 131°, the H···π vector being inclined by *ca.* 55° to the ring plane] protons in two different adjacent molecules .

In the structure of **14** one of the perchlorate anions and the included dichloromethane solvent molecule were found to be disordered, and in each case two orientations were identified.

Fig. S1 The molecular structure of ligand **7a** (50% probability ellipsoids).

Fig. S2 The molecular structure of complex **10** (50% probability ellipsoids).

Fig. S3 The molecular structure of complex **11** (50% probability ellipsoids).

Fig. S4 The molecular structure of **12** (50% probability ellipsoids).

Fig. S5 The molecular structure of the dication in **14** (50% probability ellipsoids).

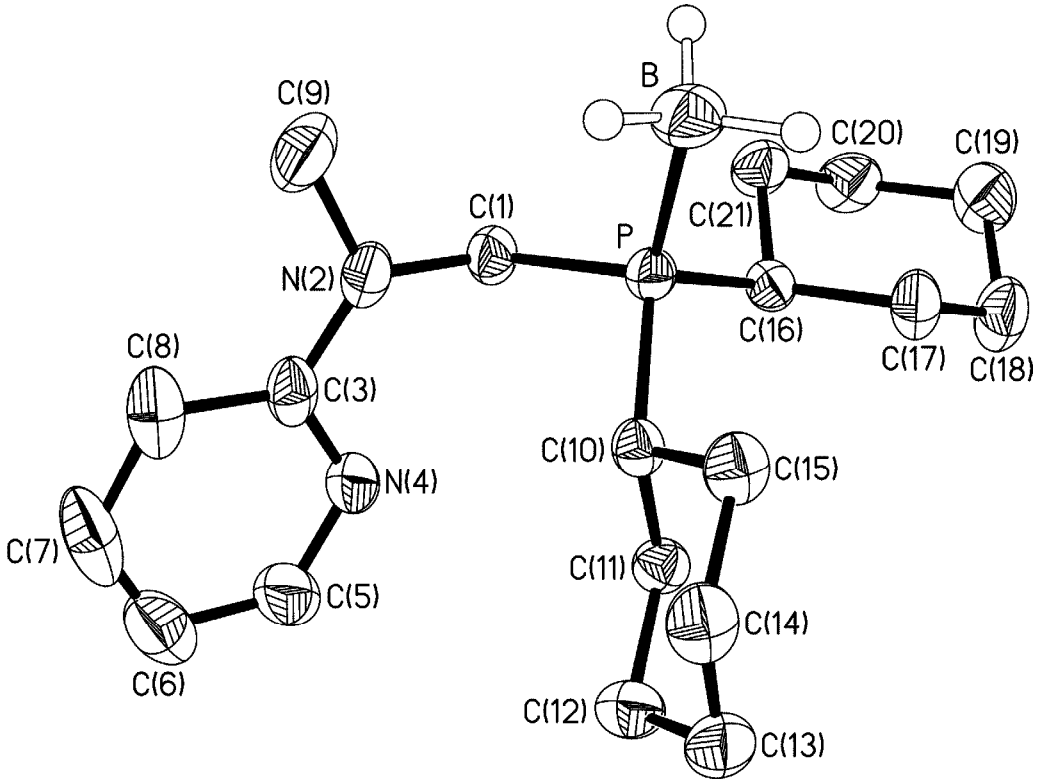

Fig. S1

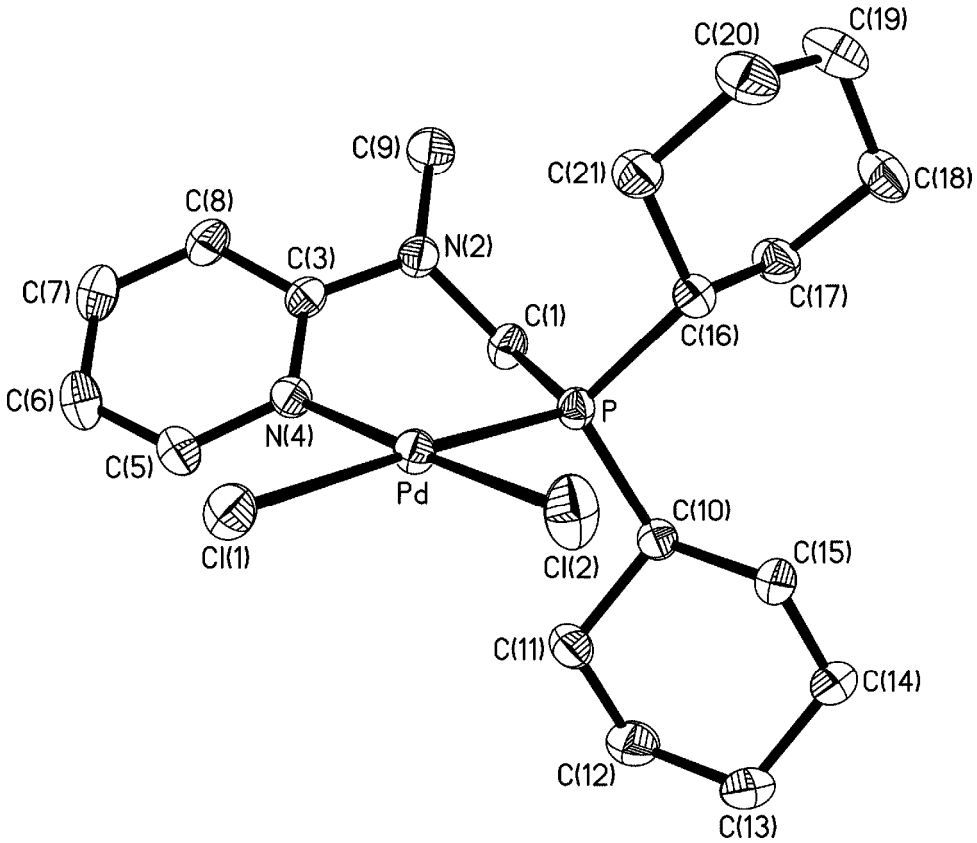

Fig. S2

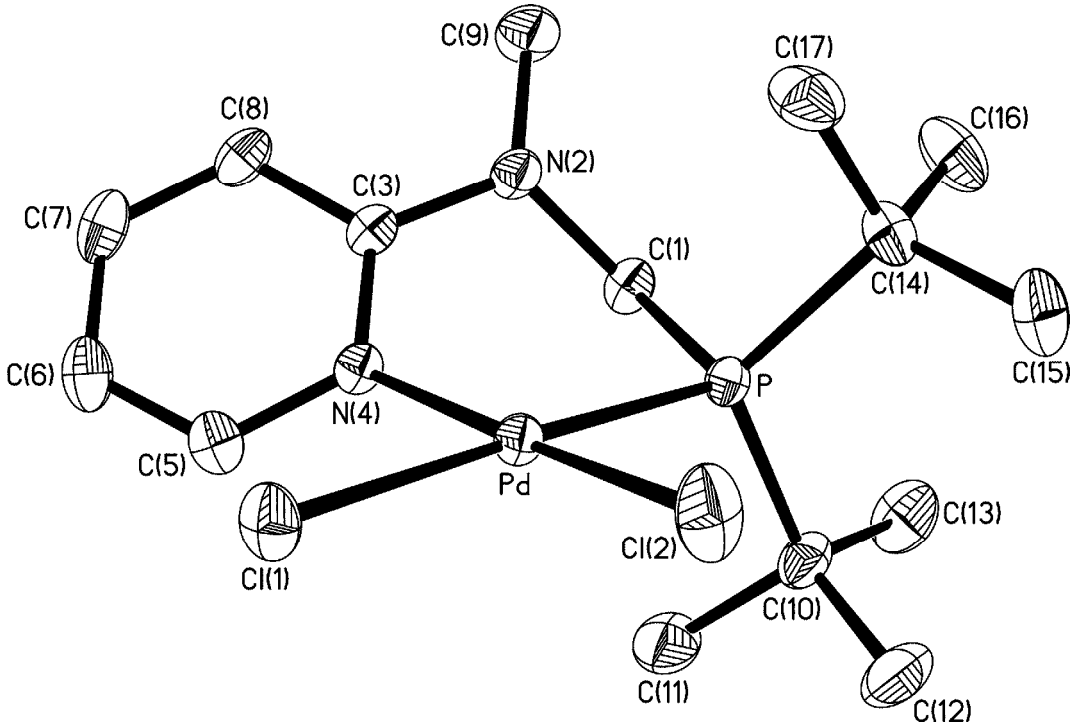

Fig. S3

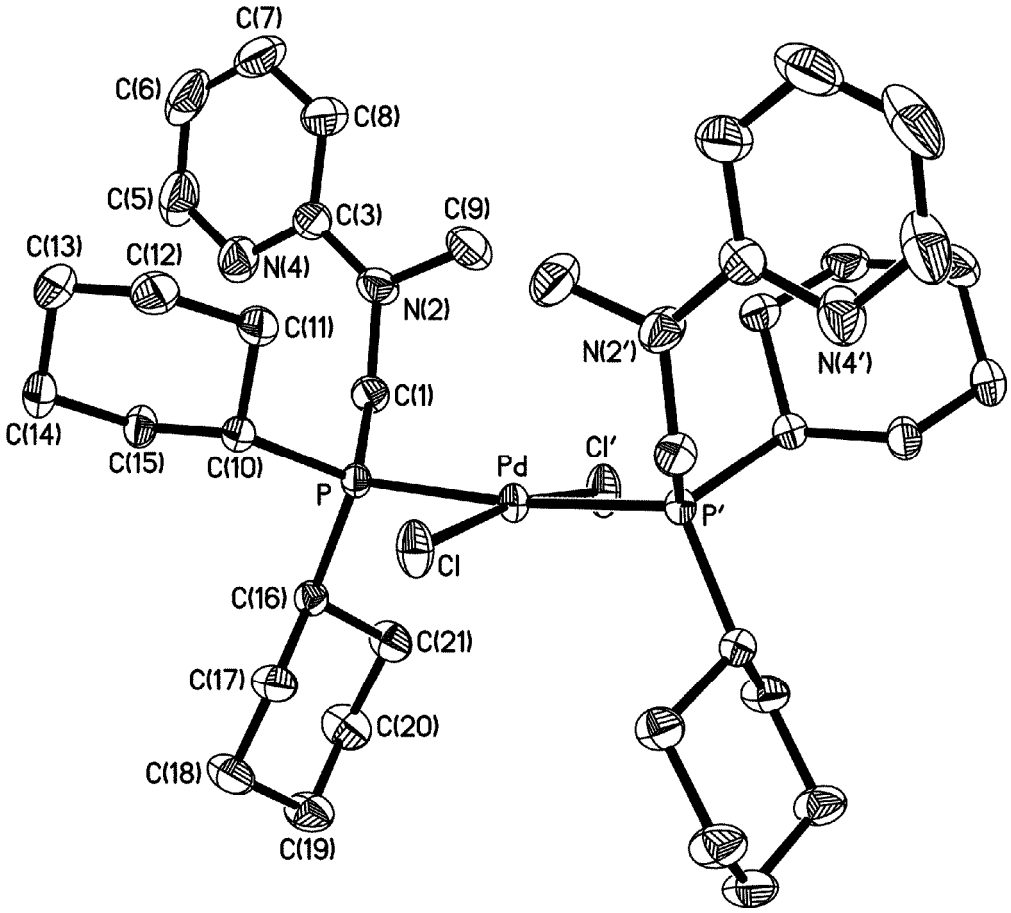

Fig. S4

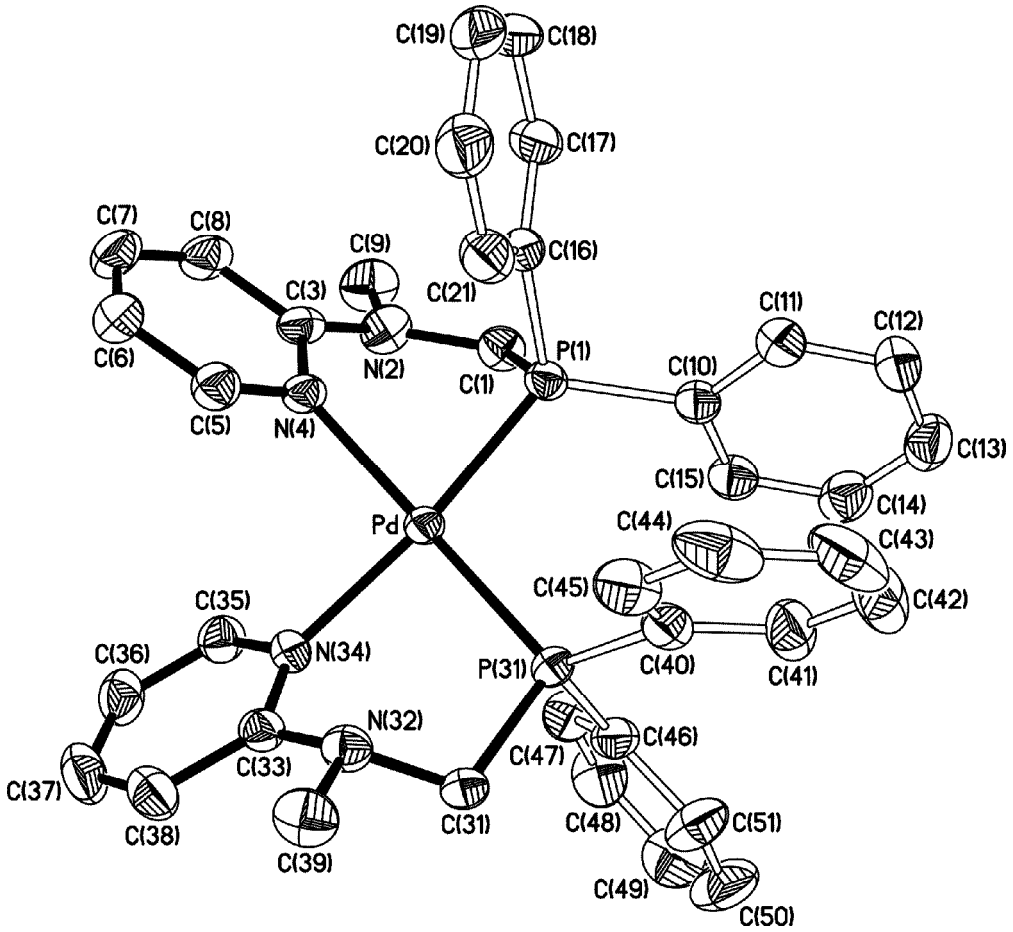

Fig. S5