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Structural distortions in Pd–MeO-Biphep and Pd–Binap aryl complexes. Anomalies induced *via* electronic effects

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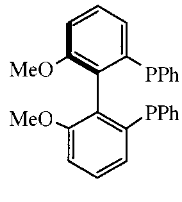
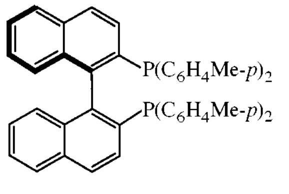
The four-coordinate complexes [PdBr(p-NCC$_6$H$_4$)(MeO-Biphep)], 1 [MeO-Biphep = 6,6′-dimethoxy-2,2′-bis(diphenylphosphino)-1,1′-biphenyl], and [PdBr(p-NC-C$_6$H$_4$)(p-tol-Binap)], 2 [p-tol-Binap = 2,2′-bis(di-p-tolylphosphino)-1,1′-binaphthyl], both distort markedly, with the former no longer square-planar, and the latter, possessing the longest recorded Pd–P bond length.

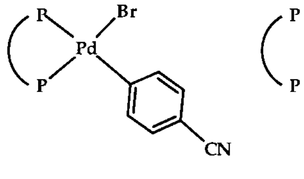
The atropisomeric chiral bidentates MeO-Biphep and Binap are recognised to be excellent auxiliaries in a number of enantioselective transformations,[1–3] including C–C coupling.[4] Pd–aryl complexes, which are intermediates in both cross-coupling and Heck chemistry,[4] arise from the oxidative addition of aryl–X compounds, X = I, Br, OTs, to Pd(0) complexes.[5–10] In connection with kinetic studies related to the enantioselective Heck reaction we recently noted[11] that aryl intermediates of the type [PdX(aryl)(MeO-Biphep)], with electron-donor groups on the aryl, are not very stable. We report here that the structures of the compounds [PdBr(p-NCC$_6$H$_4$)(MeO-Biphep)], **1**, and [PdBr(p-NCC$_6$H$_4$)(p-tol-Binap)], **2**, which are more stable, both distort markedly (but very differently) in order to accommodate the electronic pressure exerted by the aryl groups.†



MeO-Biphep



p-tol-Binap



= MeO-Biphep, **1** or p-tol-Binap, **2**

The molecular structures for **1** and **2** were determined *via* X-ray diffraction methods‡ and ORTEP views of these molecules are given in Figs. 1 and 2. Selected bond distances and bond angles are given in the captions. In compound **1** there is sufficient space for the aryl and bromide ligands; nevertheless both ligands deviate so strongly from the coordination plane defined by the two P-donors and the metal, +0.88 Å and −0.57 Å, respectively, that one can no longer speak of a square planar geometry. We envision the structure as arising *via* rotation of the P–Pd–P and Cl–Pd–Br, planes, relative to one another, and not due to a tetrahedral distortion (note that the P–Pd–P and C1L–Pd–Br angles are *ca.* 94° and 90°, respectively). The Pd–C1L separation of 2.104(3) Å is relatively long [2.04–2.06 Å is normal for MeO-Biphep[11] although, in general much shorter Pd–C(aryl) distances have been reported[12,13]]. The ring of the p-NCC$_6$H$_4$ ligand makes an angle of *ca.* 73° with the P–Pd–P plane, but seems to be somewhat bent, P2–Pd–C1L = 163°, see Fig. 1a. We find no evidence for strain due to packing effects.

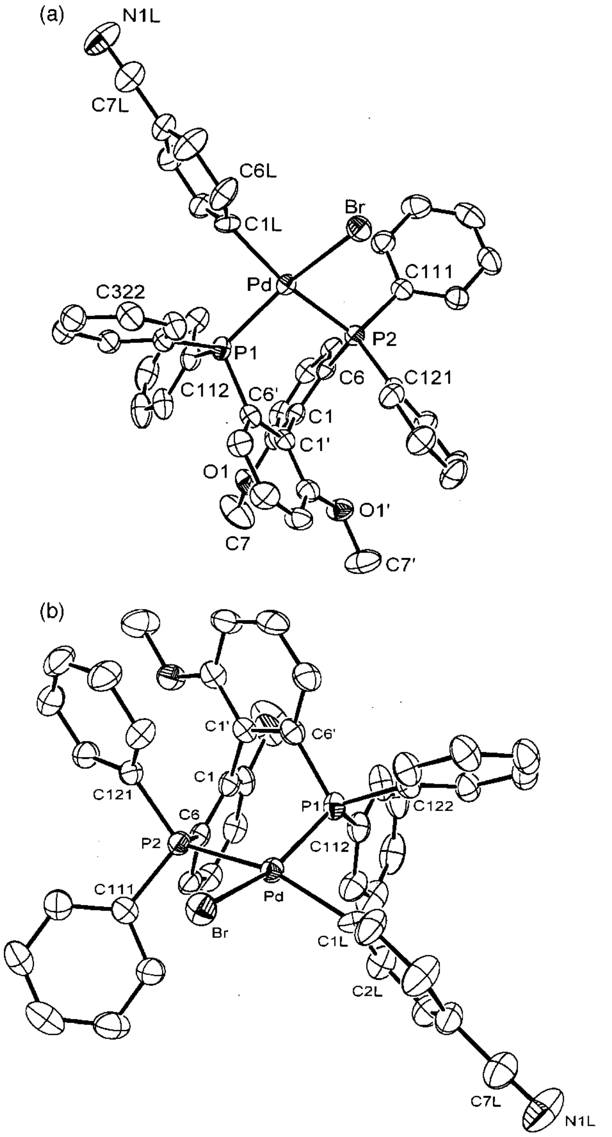


Fig. 1 ORTEP[20] views of complex **1**. (a) From above and (b) from behind (and slightly above) the p-cyanoaryl ligand. Selected bond lengths (Å) and bond angles (°) for **1**: Pd–P1 2.2700(9), Pd–P2 2.3501(9), Pd–C1L 2.104(3), Pd–Br 2.4920(4), C7L–N1 1.126(5); P1–Pd–P2 94.06(3), P2–Pd–C1L 163.02(10), P1–Pd–C1L 92.22(9), P1–Pd–Br 158.96(3), P2–Pd–Br 89.69(2), C1L–Pd–Br 90.09(9).

For the Binap complex **2** the observed coordination geometry is slightly distorted square planar, see Fig. 2. Relative to **1** the Pd–C1L bond separation is now 0.078 Å shorter, 2.026(6) Å;[14] however, a search of the Cambridge database reveals that the

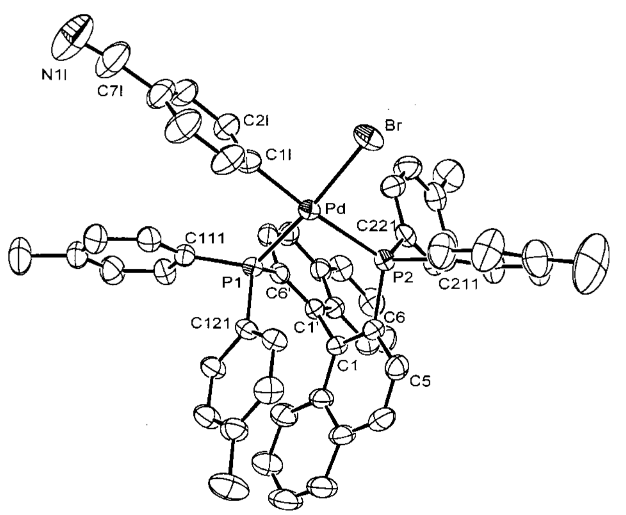
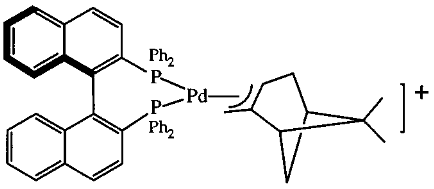


Fig. 2 ORTEP view of complex **2** looking down on the *p*-cyanoaryl ligand and the coordination plane. Selected bond lengths (Å) and bond angles (°) for **2**: Pd–P1 2.254(1), Pd–P2 2.437(1), Pd–C1L, 2.026(6), Pd–Br 2.4484(7), C7–N1 1.12(1); P1–Pd–P2 92.38(5), P2–Pd–C1L 175.6(2), P1–Pd–C1L 91.0(2), P1–Pd–Br 173.51(4), P2–Pd–Br 90.90(4), C1L–Pd–Br 85.4(2).

Pd–P2 bond, *trans* to the aryl, at 2.437(1) Å represents the longest Pd–P bond ever reported.§ For comparison, in the Binap β-pinene allyl complex [Pd(η^3-$C_{10}H_{15}$){(*R*)-(+)-Binap}][CF_3SO_3], **3**, the Pd–P distances are 2.312(3) Å and 2.347(5) Å.[15] The observed Pd–P2 bond in **1**, 2.3501(9) Å, is much shorter, but lies towards the upper end of the literature range (Pd–P separations of the order of *ca.* 2.20–2.36 Å are common[16–19]). In both **1** and **2** the *p*-CN group appears to be a normal triple bond (see captions).



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Despite the superficial similarity of the ligands, *i.e.*, biaryl-based triaryl phosphine types, the structures for **1** and **2** are very different. Whereas the extreme lengthening of the Pd–P2 bond in the Binap complex **2** arises due to good donor properties of the aryl group, the MeO-Biphep analog **1** avoids this electronic strain by strongly deviating from square planar geometry and thus weakening the Pd–C1L overlap. Given the rather novel structural results for these *p*-NCC_6H_4 aryl compounds, it is not surprising that we cannot readily isolate analogous complexes with aryl ligands which are even more electron donating, *e.g.* *p*-MeC_6H_4 and *p*-$MeOC_6H_4$.

Acknowledgements

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Notes and references

† The complexes were prepared as described in reference 11.

‡ Crystal data for compound **1**: $C_{45}H_{36}BrNO_2P_2Pd$, $M = 871.00$, orthorhombic, space group $P2_12_12_1$ (no. 18), $a = 11.4485(2)$, $b = 17.3604(1)$, $c = 19.0940(3)$ Å, $U = 3794.94(9)$ Å^3, $Z = 4$, $\mu = 16.66$ cm^{-1}, $T = 200$ K, $R1 = 0.0267$ (for 5794 unique reflections having $I > 2\sigma(I)$), 0.0354 (for all 6492 independent reflections). Crystal data for compound **2**·CH_2Cl_2: $C_{56}H_{46}BrCl_2NP_2Pd$, $M = 1052.16$, monoclinic, space group $C2$ (no. 5), $a = 29.0943(4)$, $b = 11.8671(2)$, $c = 17.2953(2)$ Å, $\beta = 116.790(3)°$, $U = 5330.51(13)$ Å^3, $Z = 4$, $\mu = 12.94$ cm^{-1}, $T = 293$ K, $R1 = 0.0419$ (for 5550 unique reflections with $I > 2\sigma(I)$), 0.0494 (for all 7049 independent reflections). CCDC reference number 186/1478.

§ *Note added at proof*: a Pd–P bond length of *ca.* 2.5 Å (*trans* to $SiCl_3$) has been observed.[21]

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