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Synthesis and electrospray mass spectrometry of palladium(II) diphosphine complexes from oxidative addition of 2-bromopyridine to Pd^0

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Oxidative addition reactions of palladium(0) phosphine complexes with 2-bromopyridine gave rise to a series of structurally distinctive complexes, namely *trans*-(N,P)-$[Pd_2Br_2(PPh_3)_2(\mu\text{-}C_5H_4N\text{-}C^2,N)_2]$ **1**, $[Pd_2(\mu\text{-}C_5H_4N\text{-}C^2,N)_2(\mu\text{-dppm})_2]Br_2$ **2**, $[Pd_2(\eta^1\text{-dppp})_2(\mu\text{-}C_5H_4N\text{-}C^2,N)_2(\mu\text{-dppp})]Br_2$ **3**, *trans*-$[\{PdBr(\eta^1\text{-}C_5H_4N\text{-}C^2)(\mu\text{-dppb})\}_n]$ **4**, *trans*-(N,P)-$[Pd_2Br_2(\mu\text{-}C_5H_4N\text{-}C^2,N)_2(\mu\text{-dppb})]$ **5** and *cis*-$[PdBr(\eta^1\text{-}C_5H_4NH\text{-}C^2)(\eta^2\text{-dppf})]Br$ **6** $[Ph_2P(CH_2)_nPPh_2$, $n = 1$(dppm), 3(dppp) or 4(dppb); dppf = $Fe(Ph_2PC_5H_4)_2$]. Similarly, *trans*-(N,P)-$[Pd_2Cl_2(\mu\text{-}C_9H_6N\text{-}C^2,N)_2(\mu\text{-dppb})]$ **7** has been obtained from 2-chloroquinoline and $[Pd(dppb)_2]$. An array of structural possibilities is envisaged based on the different co-ordination modes of the pyridine (C or/and N bonded; terminal or bridging; pyridyl, pyridine or pyridinium), phosphine (terminal, bridging or chelating) bromide (terminal or ionised) ligands. Complexes **2** and **3**, but not the others, can be obtained from phosphine exchange reactions of **1**. Complexes **5** and **6** were analysed by X-ray single-crystal crystallographic methods. The former reveals a dinuclear structure with a dppb ligand bridging diagonally two metals that are juxtaposed by two *syn*-bridging pyridyl groups. It represents an unusual dinuclear core stabilised by two types of bridging ligands of contrasting steric and geometric demands. The latter shows a cationic and mononuclear square planar palladium(II) complex containing a chelating dppf, terminal bromide and an unusual C-bonded pyridyl group with the N-site protonated. The fragmentation of these complexes was investigated by electrospray mass spectrometry under different cone voltages. Breakdown of the dinuclear framework is facilitated by addition of H–Br to the N–Pd bonds of the bridging pyridyl group.

Introduction

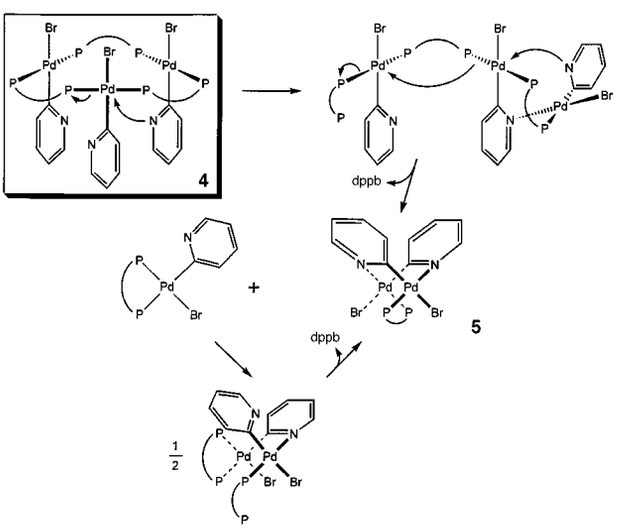
Since the turn of the century the chemistry of polymers has expanded enormously.[1] Organic bifunctional polymers containing heterocyclic rings have wide applications as they exhibit properties such as optical non-linearity[2] and anisotropic electrical conductivity.[3] Hitherto, these polymers have been used as electrochemical energy storage[4] and electrochromic devices,[5] as molecular catalysts[6] and in molecular electronics.[7] A convenient synthetic pathway for these polymers is the polymerisation of their respective monomers. The future applications of these polymers hence hinge on our ability chemically to manipulate their monomeric or oligomeric building blocks. Among the most successful methodologies for the current synthesis of these precursors are metal-catalysed hetero-coupling reactions, *e.g.* Grignard,[8] Stille[9] and Suzuki[10] couplings, in which organometallic catalyst precursors, especially palladium(0) and palladium(II) phosphine complexes, are inevitably involved. The common use of PPh_3 as supporting ligands leads to the synthesis of a range of monomeric complexes that are catalytically related. For example, oxidative addition reaction of 3- or 4-bromopyridine to $[Pd(PPh_3)_4]$ results in *trans*-$[PdBr(\eta^1\text{-}C_5H_4N\text{-}C^n)(PPh_3)_2]$ ($n = 3$ or 4),[11,12] which readily undergoes metathesis with anions such as N_3^-, NCO^-, NCS^-, $NCSe^-$, ClO_4^-, BF_4^- and PF_6^-.[13] These mononuclear complexes are generally considered as catalytically active. By a careful choice of incoming nucleophile (Nuc), one would obtain $[Pd(Nuc)(\eta^1\text{-}C_5H_4N\text{-}C^n)(PPh_3)_2]$ ($n = 3$ or 4) which could reductively eliminate NH_4C_5-Nuc as a hetero-coupled product and regenerate $[Pd(PPh_3)_2]$ as the active catalyst. Even in the cases when dinuclear complexes are formed, *e.g.* 2-bromopyridine giving *trans*-(N,P)-$[Pd_2Br_2(PPh_3)_2(\mu\text{-}C_5H_4N\text{-}C^2,N)_2]$ **1**,[13] they could break down to mononuclear complexes upon ligand exchange.[14a] The involvement of dinuclear palladium(II) complexes in the catalytic cycle is generally neglected despite their first synthesis back in 1980[12] and subsequent works.[14] Accordingly, the current understanding of the mononuclear catalytic intermediates is inadequate for $PdCl_2(P\text{–}P)$[15] which contain bidentate phosphines (P–P) such as dppe, dppp $[Ph_2P(CH_2)_3PPh_2]$ and dppf as supporting ligands. The literature is poorly developed on the structures of these catalytic intermediates and the co-ordination and structural roles of diphosphine on a dinuclear framework. In this paper, using 2-bromopyridine as a model, we examine the stabilising effects and structural influence of different diphosphines on a dinuclear skeleton. The complexes formed are characterised by X-ray single-crystal diffractometry and electrospray mass spectrometry (ESMS).

Results and discussion

Synthesis

Oxidative addition of 2-bromopyridine to $[Pd(PPh_3)_4]$ occurs readily at room temperature (r.t.) to give a near-quantitative yield of *trans*-(N,P)-$[Pd_2Br_2(PPh_3)_2(\mu\text{-}C_5H_4N\text{-}C^2,N)_2]$ **1**. The same complex was reported to be obtainable only under reflux conditions.[13] Its identity is substantiated by NMR spectroscopy and ESMS (see below). Similar reaction occurs between $[Pd_2(dppm)_3]$ and 2-bromopyridine in refluxing toluene to give $[Pd_2(\mu\text{-}C_5H_4N\text{-}C^2,N)_2(\mu\text{-dppm})_2]Br_2$ **2**. The ^{31}P NMR analysis shows two sets of triplets indicating two pairs of phosphines which are chemically distinct. The parent molecular ion was detected by ESMS analysis (*m/z ca.* 569). Complex **2** is one of the few palladium dinuclear complexes with no terminal but

four bridging ligands, namely two C- and N-bonded pyridyl and two dppm groups. It can also be obtained from the stoichiometric phosphine-exchange reaction of **1** with dppm. Similar reaction of $[Pd(dppp)_2]$ with 2-bromopyridine yields a third structural type of dinuclear complex $[Pd_2(\eta^1\text{-dppp})_2(\mu\text{-}C_5H_4N\text{-}C^2,N)_2(\mu\text{-dppp})]Br_2$ **3**. It contains three dppp ligands, two of which are pendant and one is in a diagonal-bridging mode; this is consistent with the three discrete resonances in the ^{31}P NMR spectrum. The ESMS spectrum gives a molecular peak at $m/z = 803.4$, which agrees with the dicationic configuration. Similar to **2**, phosphine exchange reaction of **1** with an excess of dppp yields **3** as the major product. Reaction between 2-bromopyridine and $[Pd(dppb)_2]$ [dppb = $Ph_2P(CH_2)_4PPh_2$] gives different products depending on the reaction temperatures. At r.t. a complex analysed to be *trans*-$[\{PdBr(\eta^1\text{-}C_5H_4N\text{-}C^2)(\mu\text{-dppb})\}_n]$ **4** resulted. Under toluene reflux the major product is *trans*-(N,P)-$[Pd_2Br_2(C_5H_4N\text{-}C^2,N)_2(\mu\text{-dppb})]$ **5**. Although the nuclearity of complex **4** is presently unclear, its role as a precursor of **5** based on a trinuclear structural model can be proposed.† Conversion is achieved by basic attack of the free pyridyl nitrogen on the neighbouring metal followed by elimination of the phosphine (Scheme 1). The by-product in this conversion, *cis*-$[PdBr(\eta^1\text{-}C_5H_4N\text{-}C^2)(\eta^2\text{-dppb})]$, can add to the yield of **5** by a simple dimerisation process with the elimination of phosphine. Similar reaction between 2-bromopyridine and $[Pd(dppf)_2]$ in refluxing toluene gives a dark red-brown complex characterised as *cis*-$[PdBr(\eta^1\text{-}C_5H_4NH\text{-}C^2)(\eta^2\text{-dppf})]Br$ **6**. The ^{31}P NMR spectrum shows two sets of doublets expected for a mononuclear structure with inequivalent phosphine sites. There is no evidence for the expected product *cis*-$[PdBr(\eta^1\text{-}C_5H_4N\text{-}C^2)(\eta^2\text{-dppf})]$. The free pyridyl nitrogen is probably very prone to protonation by a trace of HBr in the 2-bromopyridine.‡ The fact that **6** cannot be obtained from the exchange reaction of **1** with dppf also supports the formulation of **6**. Complex *trans*-(N,P)-$[Pd_2Cl_2(\mu\text{-}C_9H_6N\text{-}C^2,N)_2(\mu\text{-dppb})]$ **7**, the chloroquinolyl analogue of **5**, is isolated from a r.t. reaction between $[Pd(dppb)_2]$ and 2-chloroquinoline.



Scheme 1

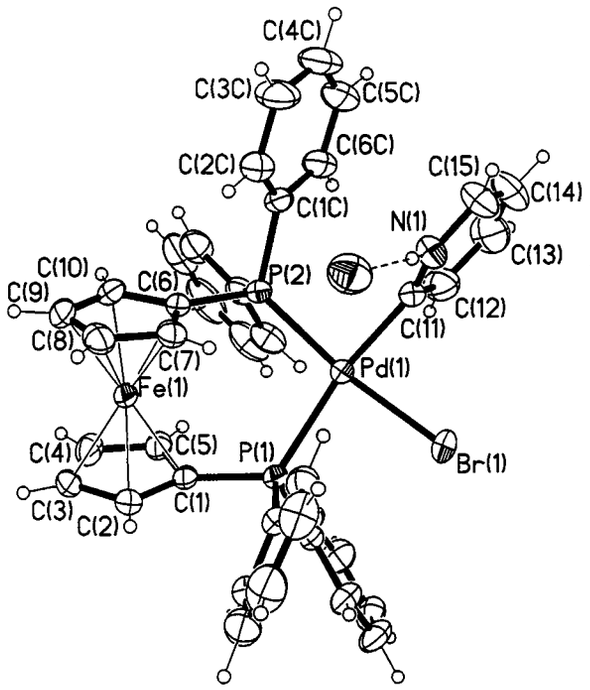


Fig. 1 An ORTEP drawing (50% probability level) of the molecular structure of *cis*-$[PdBr(\eta^1\text{-}C_5H_4NH\text{-}C^2)(\eta^2\text{-dppf})]Br$ **6**.

Structures

The isolated complexes illustrate a wide range of structural variations. All six complexes **1**–**6** are structurally distinct whereas **5** and **7** are isostructural. Complexes **1**–**3** and **5** are dinuclear with two bridging pyridyl ligands and none to two bridging phosphine ligands. Single-crystal X-ray diffraction analysis of **6** reveals a mononuclear d^8 cation with a chelating dppf and an unusual C-co-ordinated pyridyl with the nitrogen site protonated giving a ligand best described as a neutral pyridinium (Fig. 1, Table 1).

The close contact of N(1)H···Br(2) [N(1)–H(11) 0.860, Br(2)–H(11) 2.367(4) Å; N(1)–H(11)–Br(2) 177.61(9)°] strongly supports the protonated model. The established higher *trans* influence of the Pd–C bond weakens significantly the opposite Pd–P bond [2.3863(8) Å] which faces Br. A similar phenomenon has been observed in a *cis*-[PdBr(aryl)(dppe)] complex.[16] The P–Pd–P chelate angle [102.08(3)°] is comparable to those found in other square-planar complexes [97.5(1)–104.4(2)°].[17] The staggered conformation of the ferrocenyl rings [τ 40.8(6)°] is consistent with those in other square-planar chelates.[18] The pyridyl ligand is found primarily in the forms of C-bonded pyridyl and pyridinium and C,N-bonded pyridyl. It is a terminal ligand C-bonded in both **4** and **6**, with **6** having the nitrogen end protonated. The phosphine is bridging in most cases (**2**, **3**, **4**, **5** and **7**) but chelating in **6** and unidentate in **3**. In **5**, the bridging phosphine is in the diagonal-bridging mode *trans* to the nitrogen end of pyridyl, while for **2** the diphosphine displays the *syn*-bridging mode and is necessarily *trans* to both C and N ends. In **3** the bridging dppp is *trans* to the N-donors whilst the terminal ones are opposite the carbon ends. These structural variations are attributed to both electronic and steric factors. The high *trans*-directing phosphine causes the N of the bridging pyridyl to adopt the *trans*-P position. This governs the diagonal-bridging mode for dppb in **5** and accounts for the chemically equivalent phosphine sites on a hetero-bridged system. In **3** the distinction is less obvious as there are phosphines

† The complex cannot be monomeric since the phosphine sites are chemically equivalent (^{31}P NMR). A dimeric model is possible but not likely as it would entail an unusual $[Pd_2(\mu\text{-dppb})_2]$ moiety that is geometrically constrained. A trimeric model is possible as it has a reasonable mechanistic path for the generation of a monomeric and dimeric (**5**) pyridyl complexes under ESMS conditions (described later) although there is no definitive experimental support. The ESMS spectrum at 5 V only reveals $dppbO_2$, $M + H^+$ and $2M + H^+$. Addition of the pyridine only breaks up the "oligomer" and gives monomeric species.

‡ One alternative is that oxidation gives rise to *cis*-$[Pd(\eta^2\text{-}C_5H_4\text{-}N\text{-}C^2,N)(dppf)]Br$ which rapidly undergoes H–Br addition across the N–Pd bond (in a manner similar to the formation of **2a** from **2** described later) to relieve the stress on the strained chelate.

Table 1 Selected bond lengths (Å) and angles (°) for (a) *trans*-(N,P)-[Pd_2Br_2(μ-C_5H_4N-C^2,N)$_2$(μ-dppb)]·MeCN **5** and (b) *cis*-[PdBr(η^1-C_5H_4NH-C^2)(η^2-dppf)]Br·0.5MeOH **6**

(*a*)

Pd(1)–C(6)	1.993(4)	Pd(1)–N(1)	2.093(3)
Pd(1)–P(2)	2.2609(10)	Pd(1)–Br(1)	2.5197(5)
Pd(2)–N(2)	2.096(3)	Pd(2)–C(1)	2.003(4)
Pd(2)–Br(2)	2.5196(5)	Pd(2)–P(1)	2.2678(11)
N(1)–C(5)	1.352(5)	N(1)–C(1)	1.352(5)
N(2)–C(10)	1.348(5)	N(2)–C(6)	1.356(5)
C(6)–Pd(1)–N(1)	87.4(2)	C(6)–Pd(1)–P(2)	92.52(12)
N(1)–Pd(1)–P(1)	169.31(9)	C(6)–Pd(1)–Br(1)	173.78(11)
N(1)–Pd(1)–Br(1)	91.12(9)	P(1)–Pd(1)–Br(1)	90.95(3)
C(6)–Pd(1)–Pd(2)	64.29(12)	N(1)–Pd(1)–Pd(2)	61.63(9)
P(1)–Pd(1)–Pd(2)	108.83(3)	Br(1)–Pd(1)–Pd(2)	119.28(2)
C(1)–Pd(2)–N(2)	87.10(14)	C(1)–Pd(2)–P(2)	93.29(11)
N(2)–Pd(2)–P(2)	170.06(10)	C(1)–Pd(2)–Br(2)	172.35(11)
N(2)–Pd(2)–Br(2)	90.62(9)	P(2)–Pd(2)–Br(2)	90.22(3)
C(1)–Pd(2)–Pd(1)	64.30(12)	N(2)–Pd(2)–Pd(1)	61.64(10)
P(2)–Pd(2)–Pd(1)	109.68(3)	Br(2)–Pd(2)–Pd(1)	120.72(2)

(*b*)

Pd(1)–C(11)	2.037(3)	Pd(1)–P(2)	2.2837(8)
Pd(1)–P(1)	2.3863(8)	Pd(1)–Br(1)	2.4695(4)
P(1)–C(1)	1.812(3)	P(2)–C(6)	1.804(3)
N(1)–C(11)	1.341(5)	N(1)–C(15)	1.353(5)
N(1)–H(11)	0.860	Br(2)–H(11)	2.367(4)
C(11)–Pd(1)–P(2)	87.50(9)	C(11)–Pd(1)–P(1)	169.77(9)
P(1)–Pd(1)–P(2)	102.08(3)	C(11)–Pd(1)–Br(1)	84.50(9)
P(2)–Pd(1)–Br(1)	172.00(2)	P(1)–Pd(1)–Br(1)	85.91(2)
N(1)–H(11)–Br(2)	177.61(9)		

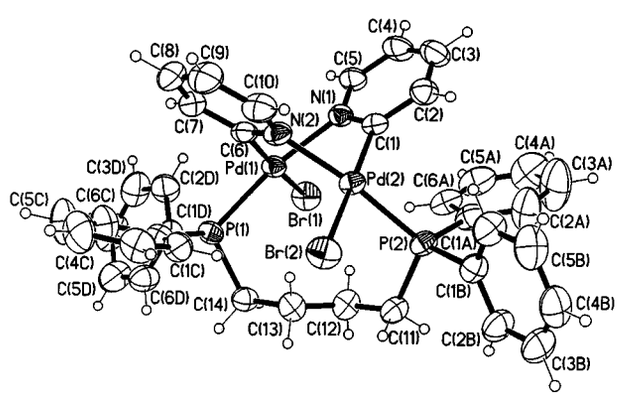
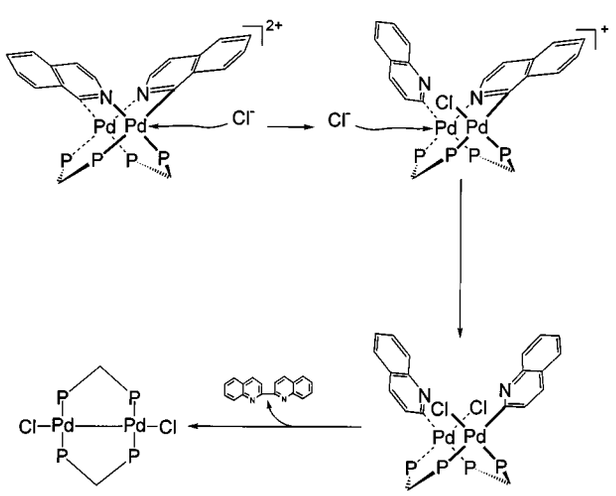


Fig. 2 An ORTEP drawing (50% probability level) of the molecular structure of *trans*-(N,P)-[Pd_2Br_2(μ-C_5H_4N-C^2,N)$_2$(μ-dppb)] **5**.

trans to both carbon and nitrogen ends. The two bridging pyridyl rings juxtapose the metal atoms and determine the Pd–Pd separation, thereby restricting the type of diphosphine ligands that are suitable for the diagonal-bridging mode. The long and flexible carbon skeletal chains of dppp and dppb do not favour a *syn*-bridge conformation but permit the diagonal-bridge formation.

These ideas are illustrated in the single-crystal X-ray molecular structure of **5** (Fig. 2). It is an unusual dinuclear structure showing how two sterically contrasting bridging ligands can be accommodated within a dinuclear framework. With the two square-planar palladium atoms locked by two pyridyl bridges in a *syn* conformation [dihedral angle between the Pd(1)–C(6)–N(2)–Pd(2) and Pd(1)–N(1)–C(1)–Pd(2) planes is 77.06(7)°], the dppb ligand takes advantage of its long alkyl chain by traversing in a diagonal-bridging mode. This forces the Br(1)–Pd(1)···Pd(2)–Br(2) torsional angle to twist from an ideal 0 to 88.11(4)°. As a result the phosphines fit into the Pd_2 pocket and are chemically equivalent, which is consistent with the solution NMR data. The similar Pd–P bond lengths [2.2609(10) and 2.2678 (11) Å] (and similar Pd–Br and Pd–N bond lengths on both palladium planes) also reflect such parity. It is notable that the Pd–Br [2.5197(5) Å] bond is significantly longer than that in **6** [2.4695(4) Å]. This is indicative of the higher *trans* influence of the pyridyl carbon in **5** (compared to the phosphino group in **6**) and suggests that the terminal bromide is susceptible to ligand exchanges. This is verified in the formation of **2** and **3** from **1** and is an important consideration in the design of these Pd_2 species as catalysts for hetero-couplings. Comparison of the crystal structures of **1** and **5** shows that the diphosphine ligand increases the torsional twist of Br–Pd···Pd–Br. The compounds dppm and dppf, on the other hand, are too short and crowded respectively to fit into the diagonal-bridge 'cavity' and hence their equivalents of **5** cannot be obtained. For entropic reasons it is not favourable for **5** to take up two additional dangling dppb ligands like that in **3**. The pin-wheel-like structure of **2** is stabilised by four bridging ligands of comparable steric requirements. There is little driving force for such a structure to disrupt and give way to any structure with dangling phosphines. The steric demand of dppf favours a chelating mode that provides an impetus for **6** to be mononuclear.

Although we have successfully assembled a quinolyl derivative of a tribridged system, *viz.* **7**, it is worth noting that refluxing 2-chloroquinoline with [Pd_2(dppm)$_3$] in toluene, contrary to what is found with **2** or **7**, does not result in the isolation of any quinolyl complex but an unexpected product, [Pd_2Cl_2(μ-dppm)$_2$]. One possible explanation is that, although similar oxidative addition can occur, a quinolyl-bridged structure analogous to that of **2** or **7** could break down under forcing conditions (Scheme 2). Chloride attack would open the bridge



Scheme 2

by converting a C,N-bonded to a C-bonded quinolyl group. Intramolecular reductive elimination would follow and yield 2,2′-biquinoline and the observed product, [Pd_2Cl_2(μ-dppm)$_2$]. Similar Pd^I–Pd^I complexes of the dppp, dppb and dppf analogues are rare and their synthesis from this path is a subject of our current investigation.

These results suggest that a slight change in the skeletal property of the diphosphine would have a significant influence on the dinuclear framework. This intricate influence is manifested in different bonding modes of the phosphines, which result in different structures. For a diphosphine that favours a chelating mode the dinuclear unit can break down to a mononuclear complex, as witnessed in **6**. Attempts to synthesize the dppe analogue of **5** by oxidative addition have so far been unsuccessful. This is reminiscent of the sensitivity of the dinuclear structure to its diphosphine skeletal residue. In the phosphine exchange reactions, dppm and dppp react smoothly with **1** to give **2** and **3** respectively. However, dppb, dppf and dppe, whose co-ordinating ability is not known to be weaker, do not show

any activity. These differences emphasise the stability bridging of dppm (*e.g.* in A-frame type complexes) and possible isolation of the unidentate mode of dppp due to its optimum chain length. The similar ease of replacement of PPh_3 or Br^- in **1** makes structural prediction of any ligand-exchanged products difficult.

Among all the complexes isolated, only **6** is mononuclear. Preliminary results indicate that metathesis (and deprotonation) of **1** with $Li^+(C_4H_3S)^-$ (C_4H_3S = 2-thienyl) gives *trans*-(N,P)-$[Pd_2(\eta^1\text{-}C_4H_3S)_2(PPh_3)_2(\mu\text{-}C_5H_4N\text{-}C^2,N)_2]$ which undergoes thermolysis in toluene to give 2-thienylpyridine.[19] This suggests that at least some of the many known Pd-catalysed hetero-coupling reactions do not proceed through mononuclear intermediates, especially when the phosphines used are bidentate, and that the dinuclear complexes isolated in this work are catalytically significant.

Electrospray mass spectrometry

The emerging importance of ESMS as a soft ionisation mass spectrometry for organometallic complexes is evident.[20] In this work it is used to investigate the dinuclear-to-mononuclear breakdown of the Pd_2 species and unveil the various fragmentation possibilities of a dinuclear core. The information thus obtained would help to understand the Pd-catalysed coupling mechanisms and design of new catalysts using diphosphines as ligand support. Similar use of ESMS to observe catalytic intermediates in the Pd^0-catalysed Suzuki coupling has been reported.[21] At a very low cone voltage of 5 V, both monocationic *trans*-(N,P)-$[Pd_2Br(MeCN)(PPh_3)_2(\mu\text{-}C_5H_4N\text{-}C^2,N)_2]^+$ **1a** (m/z = 1013.9) and dicationic species *trans*-(N,P)-$[Pd_2(MeCN)_2(PPh_3)_2(\mu\text{-}C_5H_4N\text{-}C^2,N)_2]^{2+}$ **1b**, (m/z = 487.9), from MeCN displacement of Br in **1**, are observed with the latter as the dominant species (Fig. 3). The displacement of halide and subsequent co-ordination of MeCN to the parent fragment is a common phenomenon in ESMS.[22] The BF_4^- salt of **1b** was independently synthesized and its ESMS spectra analysed. They generally agree with those obtained from **1** and support that **1b** is an essential fragmentation product of **1**. At 20 V ligand fragmentation begins to occur, giving rise to $[Pd_2(PPh_3)_2(\mu\text{-}C_5H_4N\text{-}C^2,N)_2]^{2+}$ **1c** (m/z = 446.3) and $[Pd_2(MeCN)(PPh_3)_2(\mu\text{-}C_5H_4N\text{-}C^2,N)_2]^{2+}$ **1d** (m/z = 467.4). The preferred dissociation of Br^- and MeCN suggests that the bond strength of Pd–Y decreases in the order Y = PPh_3 > MeCN > Br^-. At 30 V the amount of **1c** and **1d** increases and **1c** becomes the dominant species. A species **1e** (m/z = 340.4) is formed whose isotope pattern suggests a phosphonium cation $[Ph_3PC_5H_4N]^+$, formed by dissociative coupling between the phosphine and pyridyl ligands. At 40 V fragmentation to monopalladium species occurs. The peak of **1b** is overshadowed by the monomeric ion $[Pd(MeCN)(C_5H_4N)(PPh_3)]^+$ **1f**, having the same m/z value but peaks separated by 1 mass unit, and **1c** by peaks due to $[Pd(C_5H_4N)(PPh_3)]^+$ **1g**. The pyridyl ligand remains intact even at 40 V, which supports C-bonded[13,14b,23] rather than the generally weaker N-bonded pyridine. Another new species, $[Pd_2Br(C_5H_4N)_2(PPh_3)_2]^+$ **1h**, at m/z = 972.4 also surfaces at this high voltage. These results are consistent with the general observation that increasing the cone voltage results in ions of lower charge. These experiments provide unequivocal support that the dinuclear structure is maintained in solution. Dissociation of Br^- and MeCN occurs prior to the monomerisation through cleavage of the bridging pyridyl groups. Bromide dissociation is most facile and is probably assisted by the MeCN present. Similar results have been observed for other metal phosphine–halide complexes.[24] To substantiate the latter point, the ESMS spectra of **1** were recorded with the sample solution doped with a few drops of pyridine. As expected, species arising from bromide/acetonitrile replacement by pyridine, *viz. trans*-(N,P)-$[Pd_2Br(\eta^1\text{-}C_5H_5N\text{-}N)(PPh_3)_2(\mu\text{-}C_5H_4N\text{-}C^2,N)_2]^+$ **1i** (m/z = 1051.5) {and its MeCN substitution complex,

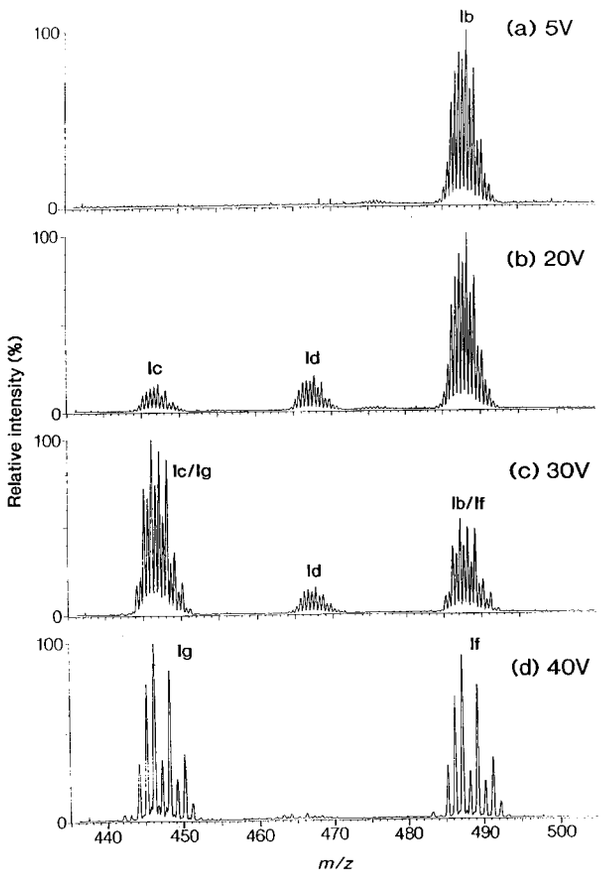
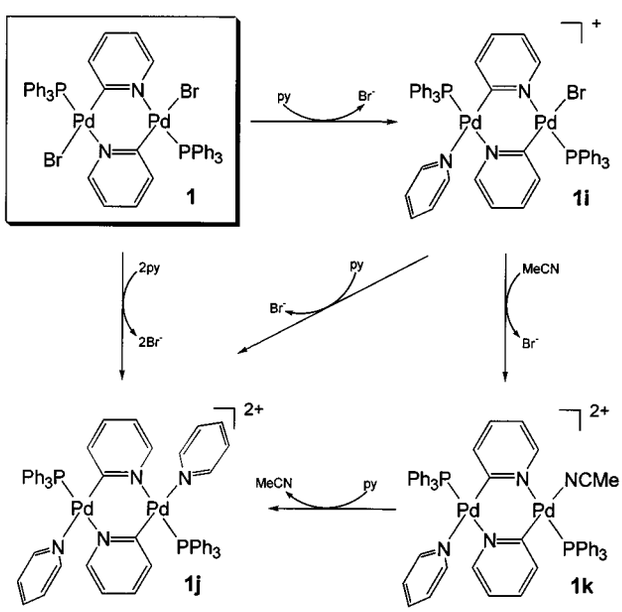


Fig. 3 Positive-ion electrospray mass spectra of complex **1** in MeCN–water solvent (1 : 1 v/v) at cone voltages of (a) 5, (b) 20, (c) 30 and (d) 40 V. The spectra show the formation of the bis(acetonitrile) dication **1b** at low cone voltages, which loses MeCN ligands (giving **1d** and **1c**) and fragments to the monomeric species **1f** and **1g** as the cone voltage is raised.



Scheme 3

trans-(N,P)-$[Pd_2(MeCN)(\eta^1\text{-}C_5H_5N\text{-}N)(PPh_3)_2(\mu\text{-}C_5H_4N\text{-}C^2,N)_2]^{2+}$ **1k** (m/z = 507.0)} and *trans*-(N,P)-$[Pd_2(\eta^1\text{-}C_5H_5N\text{-}N)_2(PPh_3)_2(\mu\text{-}C_5H_4N\text{-}C^2,N)_2]^{2+}$ **1j** (m/z = 525.5) were detected (Scheme 3). These results suggest a rich ligand replacement chemistry in **1** which can be developed in line with the catalytic initiatives.

The parent ion of complex **2** (m/z = 569) was detected as a

minor species at low cone voltage (5 V). The occurrence of two major peaks (m/z = 609.1 and 1217.7) merits special comment. The former peak is attributed to $[Pd_2H(Br)(C_5H_4N)_2(dppm)_2]^{2+}$ **2a**, which is formed from protonation of **2**, while the latter is most likely an ion pair of **2** + Br^-. The parent ion of **3** (m/z = 803.4) was detected at 5 V. The presence of three different types of ligands, *viz.* bridging pyridyl, bridging phosphine and unidentate phosphine, creates a number of possibilities for ligand transformation and molecular fragmentation. A large number of molecular peaks observed at such a low cone voltage supports this projection. Similar to **2**, complex **3** readily adds H^+Br^- to give $[Pd_2H(Br)(C_5H_4N)_2(dppp)_3]^{2+}$ **3a** (m/z = 843.3), $[Pd_2H_2Br_2(C_5H_4N)_2(dppp)_3]^{2+}$ **3b** (m/z = 884.5), $[PdH(Br)(C_5H_4N)(dppp)]^+$ **3c** (m/z = 677.5) and $[PdH(Br)(C_5H_4N)(dppp)_2]^{2+}$ **3d** (m/z = 1089.9). Chelation of one of the dangling phosphines in **3** could lead to an immediate rupture of the phosphine bridge which triggers the splitting of **3** to two mononuclear fragments: $[Pd(C_5H_4N)(dppp)_2]^{2+}$ **3f** (m/z = 1007.8) and $[Pd(C_5H_4N)(dppp)]^{2+}$ **3g** (m/z = 595.6). In the presence of trace H^+Br^-, and especially at higher voltages (*e.g.* 40 V), the amount of **3d**, **3f** and **3g** would decrease while that of **3c** is observed to increase relatively. Species **3c** is thus a possible sink in a series of acid-promoted fragmentations. As it is structurally identical to **6**, detection of **3c** together with its precursors under ESMS conditions provides a mechanistic mapping for the formation of **6** under synthetic conditions. Ligand displacement of dppp in **3** by Br^- giving $[Pd_2Br(C_5H_4N)_2(dppp)_2]^+$ **3e** (m/z = 1433.8) is also evident.

At 5 V, H^+Br^- elimination from complex **6** generates $[Pd(C_5H_4N)(dppf)]^+$ **6a** (m/z = 737.4); dimeric species corresponding to formulae $[Pd_2HBr_2(C_5H_4N)_2(dppf)_2]^+$ **6b** (m/z = 1637.7) and $[Pd_2H_2Br_3(C_5H_4N)_2(dppf)_2]^+$ **6c** (m/z = 1718.0) are also observed. The protonation site and hence the structures of these species are uncertain. At 20 V a fresh species $[Pd(C_5H_4NH)(dppf)]^{2+}$ **6d** (m/z = 369.5) is detected, which can either be formed from **6** through a bromide dissociation or **6a** through protonation. As the cone voltage is increased to 80 V, **6d** disappears and **6a** emerges as the dominant species.

Conclusion

Our work demonstrated that the structures of the palladium(II) pyridyl complexes are highly sensitive to the supporting phosphines. Although their structures are not easily predictable, they usually represent a compromise of conflicting demands of the diphosphine and pyridyl ligands. In some cases the resultant complexes arise from a series of molecular rearrangements whose mechanisms are complex and unknown. Based on the products formed under ESMS conditions, one can gain some valuable insight on the ligand transformation and coordination mode changes during the molecular rearrangement process. Although the ESMS data alone cannot provide definitive structural proof of various transient species detected, a meaningful discussion on the structural changes can be presented when supported by synthetic and crystallographic data. Collectively, this information provides a platform for us to understand the formation mechanism of the complexes concerned.

Experimental

General procedures

All reactions involving light-sensitive compounds were performed shielded from light. Unless stated otherwise, all reactions were performed under a positive pressure of purified argon. All ^1H NMR spectra were recorded at 300 MHz at 25 °C on a Bruker ACF 300 spectrometer. Chemical shifts are reported in ppm to high frequency with Me_4Si as internal standard for ^1H NMR spectra. The ^{31}P NMR spectra were recorded at 121.39 MHz with 85% H_3PO_4 as external reference. Elemental analyses were performed by the Microanalytical Laboratory staff of the Department of Chemistry in the National University of Singapore. The facile solvation of many dppf (other diphosphines) complexes precludes an accurate microanalysis of some complexes.[25] All solvents were of analytical grade and freshly distilled before use. All chemical reagents were purchased commercially and used as received. The complexes $[Pd(PPh_3)_4]$, $[Pd_2(dppm)_3]$, $[Pd(dppp)_2]$, $[Pd(dppb)_2]$ and $[Pd(dppf)_2]$ were prepared by the literature methods with slight modification.[26]

Electrospray mass spectrometry

Electrospray mass spectra were recorded using a VG Platform II instrument, using MeCN–water (1:1) or MeOH as the mobile phase solvent. Cone voltages were typically varied from 5 to 80 V in order to investigate the effect of higher voltages on fragmentation pathways of the various compounds observed. The peaks in the ESMS are identified by the most intense m/z value within the isotopic mass distribution. Further details of the experimental set-up used are available elsewhere.[27] Isotope patterns were recorded under high-resolution conditions for all major ions and compared with theoretical patterns obtained using the Isotope program.[28] In all cases there was good agreement between the experimental and calculated isotopic mass distributions.

Syntheses

***trans*-(N,P)-[$Pd_2Br_2(PPh_3)_2(\mu$-C_5H_4N-C^2,$N)_2$] 1.** Freshly prepared $[Pd(PPh_3)_4]$[26] [obtained *in situ* from $PdCl_2$ (1.000 g, 5.64 mmol)] was dissolved in toluene and 2-bromopyridine (1.620 g, 10.25 mmol) added slowly. The resulting mixture was stirred for 2 h, resulting in the formation of a yellow-green suspension. The product was filtered off and washed thoroughly with an excess of diethyl ether before recrystallisation from chloroform–hexane (2.91 g, 98%) (Found: C, 52.6; H, 3.8; Br, 13.5; N, 2.8; P, 5.8; Pd, 19.8. $C_{23}H_{19}BrNPPd$ requires C, 52.5; H, 3.7; Br, 15.2; N, 2.7; P, 5.9; Pd, 20.2%). $\delta_P(CDCl_3)$ 29.8 (s).

[$Pd_2(\mu$-C_5H_4N-C^2,$N)_2(\mu$-dppm$)_2$]Br_2 2. 2-Bromopyridine (0.724 g, 4.58 mmol) was added to a toluene solution of $[Pd_2(dppm)_3]$[26] [obtained *in situ* from $PdCl_2$ (0.310 g, 1.75 mmol)]. The resulting mixture was refluxed for *ca.* 1 d after which light yellow crystals were formed. The mixture was filtered and the crystals washed with an excess of toluene and diethyl ether and recrystallised from methanol (0.96 g, 85%) (Found: C, 54.1; H, 4.1; Br, 15.5; N, 2.1; P, 9.3; Pd, 13.0. $C_{30}H_{26}BrNP_2Pd$ requires C, 55.5; H, 4.0; Br, 12.3; N, 2.2; P, 9.6; Pd, 16.4%). $\delta_C(CD_3OD)$ 152.6 (C^2). $\delta_P(CD_3OD)$ 11.8 (t) and 3.5 (t) [J(P–P) = 30 Hz].

[$Pd_2(\eta^1$-dppp$)_2(\mu$-C_5H_4N-C^2,$N)_2(\mu$-dppp$)$]Br_2 3. Freshly prepared $[Pd(dppp)_2]$[26] [obtained *in situ* from $PdCl_2$ (0.182 g, 1.02 mmol)] was dissolved in toluene and 2-bromopyridine (0.178 g, 1.13 mmol) added slowly. The resulting mixture was refluxed for 2 h, resulting in the formation of off-white crystals. The crystals were filtered off, washed with an excess of toluene and diethyl ether and recrystallised from methanol (0.90 g, 99%) (Found: C, 62.2; H, 5.2; Br, 9.5; N, 1.7; P, 11.3; Pd, 10.2. $C_{91}H_{86}Br_2N_2P_6Pd_2$ requires C, 61.9; H, 4.9; Br, 9.1; N, 1.6; P, 10.5; Pd, 12.1%). $\delta_C(CD_3OD)$ 183.5 (C^2). $\delta_P(CD_3OD)$ 12.9 (dd) [^2J(P–P) 330, ^3J(P–P) 35], 3.4 (dd) [^2J(P–P) 330, ^3J(P–P) 54 Hz] and −4.5 (unresolved multiplets).

***trans*-[{PdBr(η^1-C_5H_4N-C^2)(μ-dppb)}$_n$]·C_6H_5Me 4.** 2-Bromopyridine (0.604 g, 3.82 mmol) was added to a toluene solution of $[Pd(dppb)_2]$[26] [obtained *in situ* from $PdCl_2$ (0.184 g, 1.04 mmol)]. The resulting mixture was stirred at r.t. until bright yellow crystals were precipitated. After filtration the crystals

were washed with an excess of toluene and diethyl ether and recrystallised from methanol–diethyl ether (0.37 g, 75%) (Found: C, 56.5; H, 5.0; Br, 11.5; N, 1.9; P, 7.9; Pd, 14.8. $C_{33}H_{32}BrNP_2Pd$ requires C, 57.4; H, 4.7; Br, 11.6; N, 2.0; P, 9.0; Pd, 15.4%). $\delta_C(CDCl_3)$ 131.7 (C^2). $\delta_P(CDCl_3)$ 32.8 (s).

***trans*-(N,P)-[Pd$_2$Br$_2$(μ-C$_5$H$_4$N-*C*^{2},*N*)$_2$(μ-dppb)] 5.** 2-Bromopyridine (0.604 g, 3.82 mmol) was added to a toluene solution of [Pd(dppb)$_2$][26] [obtained *in situ* from $PdCl_2$ (0.184 g, 1.04 mmol)]. The resulting mixture was refluxed until light yellow crystals were precipitated. After filtration the crystals were washed with an excess of toluene, methanol and diethyl ether. The product was recrystallised from dichloromethane–pentane (0.37 g, 75%) (Found: C, 47.1; H, 3.9; Br, 23.0; N, 3.3; P, 6.4; Pd, 18.7. $C_{19}H_{18}BrNPPd$ requires C, 47.9; H, 3.8; Br, 16.7; N, 3.0; P, 6.5; Pd, 22.3%). $\delta_P(CDCl_3)$ 25.2 (s).

***cis*-[PdBr(η^1-C$_5$H$_4$NH-*C*^{2})(η^2-dppf)]Br·0.5H$_2$O 6.** 2-Bromopyridine (0.433 g, 2.74 mmol) was added to a toluene solution of [Pd(dppf)$_2$][26] [obtained *in situ* from $PdCl_2$ (0.405 g, 2.28 mmol)]. The resulting mixture was refluxed until deep red crystals were precipitated from an indigo solution (about 2–3 d). After filtration, the crystals were washed with an excess of toluene and diethyl ether and recrystallised from methanol–diethyl ether (0.14 g, 14%) (Found: C, 51.5; H, 3.7; Br, 14.7; N, 1.6; P, 7.5; Fe, 6.6; Pd, 12.3. $C_{39}H_{33}Br_2FeNP_2Pd\cdot0.5H_2O$ requires C, 51.5; H, 3.8; Br, 17.6; Fe, 6.2; N, 1.5; P, 6.8; Pd, 11.7%). $\delta_C(CDCl_3)$ 140.1 (C^2). $\delta_P(CDCl_3)$ 29.4 (d) and 14.2 (d) [^2J(P–P) 19 Hz].

***trans*-(N,P)-[Pd$_2$Cl$_2$(μ-C$_9$H$_6$N-*C*^{2},*N*)$_2$(μ-dppb)] 7.** 2-Chloroquinoline (0.210 g, 1.28 mmol) was added to a toluene solution of [Pd(dppb)$_2$][26] [obtained *in situ* from $PdCl_2$ (0.227 g, 1.04 mmol)]. The resulting mixture was stirred at r.t. for *ca.* 2 d until off-white crystals were precipitated. After filtration the crystals were washed with an excess of toluene and diethyl ether (0.05 g, 17%) (Found: C, 57.6; H, 4.3; Cl, 6.4; N, 2.5; P, 4.9; Pd, 23.3. $C_{23}H_{20}ClNPPd$ requires C, 57.2; H, 4.2; Cl, 7.3; N, 2.9; P, 6.4; Pd, 22.0%). $\delta_P(CDCl_3)$ 25.7 (s).

Complex 2 from phosphine exchange reaction between 1 and dppm in 1:1 ratio. Complex **1** (0.020 g, 1.73×10^{-2} mmol) and dppm (0.007 g, 1.73×10^{-2} mmol) were suspended in methanol and stirred at r.t. for 3 d. The resultant yellow solution was filtered, concentrated and diethyl ether was added for precipitation. The light yellow solid (complex **2**) was collected by filtration, washed with an excess of diethyl ether and dried *in vacuo* (0.02 g, 62%) (Found: C, 53.8; H, 4.6; Br, 12.3; N, 2.1; P, 8.4; Pd, 15.4. $C_{60}H_{52}Br_2N_2P_4Pd_2$ requires C, 55.5; H, 4.0; Br, 12.3; N, 2.2; P, 9.6; Pd, 16.4%). $\delta_P(CD_3OD)$ 11.8 (t) and 3.5 (t) [^2J(P–P) 30 Hz].

Complex 3 from phosphine exchange reaction between 1 and an excess of dppp. Complex **1** (0.050 g, 4.33×10^{-5} mmol) and an excess of dppp (0.098 g, 1.73×10^{-4} mmol) were dissolved in toluene and stirred at r.t. for 2 d. The resultant off-white suspension was filtered, and the residue (complex **3**) was washed with an excess of toluene and diethyl ether (0.01 g, 85%) (Found: C, 61.8; H, 4.5; Br, 7.0; N, 1.3; P, 10.6; Pd, 12.6. $C_{91}H_{86}Br_2N_2P_6Pd_2$ requires C, 61.9; H, 4.9; Br, 9.1; N, 1.6; P, 10.5; Pd, 12.1%). $\delta_P(CD_3OD)$ 12.9 (dd) [^2J(P–P) 330, ^3J(P–P) 35], 3.4 (dd) [^2J(P–P) 330, ^3J(P–P) 54 Hz] and −4.5 (unresolved multiplets).

Reaction of [Pd$_2$(dppm)$_3$] with 2-chloroquinoline. 2-Chloroquinoline (0.198 g, 1.21 mmol) was added to a fresh toluene solution of [Pd$_2$(dppm)$_3$][26] [obtained *in situ* from $PdCl_2$ (0.212 g, 1.20 mmol)]. The resulting mixture was refluxed for *ca.* 2 d to give bright orange crystals of [Pd$_2$Cl$_2$(μ-dppm)$_2$]. The crystals were collected by filtration, washed with an excess of toluene and diethyl ether and recrystallised from methanol (0.30 g, 47 %) (Found: C, 57.9; H, 4.2; Cl, 6.7; P, 8.9; Pd, 15.1. $C_{25}H_{22}ClP_2Pd$ requires C, 57.1; H, 4.2; Cl, 6.7; P, 11.7; Pd, 20.2%). $\delta_P(CDCl_3)$ −3.1 (s).

***trans*-(N,P)-[Pd$_2$(MeCN)$_2$(PPh$_3$)$_2$(μ-C$_5$H$_4$N-*C*^{2},*N*)$_2$][BF$_4$]$_2$ 1b.** The salt $AgBF_4$ (0.342 g, 1.76 mmol) was added to a fresh acetonitrile solution of complex **1** (0.853 g, 0.81 mmol). The resulting mixture was stirred at r.t. for *ca.* 2 h. The mixture was filtered and diethyl ether was added to the filtrate for precipitation (yield 0.76 g, 85%) (Found: C, 53.9; H, 4.1; B, 2.0; F, 13.8; N, 4.6; P, 5.0; Pd, 18.1. $C_{25}H_{22}BF_4N_2PPd$ requires C, 54.2; H, 4.0; B, 1.9; F, 13.3; N, 5.1; P, 5.6; Pd, 19.2%). $\delta_P(CD_3CN)$ 29.5 (s).

X-Ray crystallography

Single-crystal X-ray diffraction experiments were carried out on a Siemens SMART CCD diffractometer with a sealed tube at 23 °C and Mo-Kα radiation (λ 0.71073 Å). Preliminary cell constants were obtained from 45 frames (width of 0.3° in Ω) data. Final cell parameters were obtained by global refinements of reflections obtained from integration of all the frame data. The data were collected with a frame width of 0.3° in Ω and a counting time of 20 s per frame at a crystal-to-detector distance of 5.027 cm. The software SMART[29] was used for collecting frames of data, indexing reflections and determination of lattice parameters, SAINT[17] for integration of intensity of reflections and scaling, SADABS[30] for absorption correction and SHELXTL[31] for space group and structure determination, refinements, graphics and structure reporting.

Light yellow crystals of complex **5** were grown from a sample solution in acetonitrile and dichloromethane by slow evaporation at r.t. A suitable crystal of dimensions 0.35 × 0.25 × 0.2 mm was selected, wedged inside a glass capillary tube and flame-sealed. A total of 12 548 reflections were collected in the θ range 1.74–29.04° ($-12 < h < 13$, $-16 < k < 17$, $-22 < l < 22$). For $Z = 2$, the space group $P\bar{1}$ was chosen in the triclinic system. All the non-hydrogen atoms in the neutral molecule were refined anisotropically. One disordered molecule of acetonitrile was located in the Fourier-difference synthesis (occupancy 0.5/0.5). Ideal bond distances and angles were imposed for these acetonitrile solvates and common isotropic thermal parameters were refined for each model. A riding model was used to place the hydrogen atoms in their idealised positions. In the final least-squares refinement cycles on F^2 the model converged to $R = 0.0394$, $R' = 0.0956$, and $S = 1.042$ for 7322 reflections with $F_o > 4\sigma(F_o)$ and 437 parameters, and $R = 0.0529$ and $R' = 0.1033$ for all 8929 data. In the final Fourier-difference synthesis the electron density fluctuated in the range 0.77 to −0.84 e Å^{-3}. The top peak was associated with N(1s) at a distance of 0.48 Å. There was no shift in the final cycles. An extinction correction was refined to 0.0009(2). There is a non-crystallographic two-fold symmetry in the molecule. However, MISSYM[32] did not reveal any additional symmetry.

Reddish brown rectangular crystals of complex **6** were grown by a layering method using methanol–diethyl ether. A suitable crystal of dimensions 0.50 × 0.23 × 0.13 mm was mounted at the end of a glass fibre. A total of 12 093 reflections were collected in the θ range 2.07–29.34° ($-12 < h < 13$, $-10 < k < 14$, $-25 < l < 25$). All the non-hydrogen atoms were refined anisotropically. One disordered molecule of water was located in the Fourier-difference synthesis (occupancy 0.25/0.25). A riding model was used to place the hydrogen atoms in their idealised positions except for the water molecule. In the final least-squares refinement cycles on F^2 the model converged to $R = 0.0395$, $R' = 0.1060$, and $S = 1.036$ for 7000 reflections with $F_o > 4\sigma(F_o)$ and 434 parameters, and $R = 0.0510$ and $R' = 0.1126$ for all 8582 data. In the final Fourier-difference synthesis

Table 2 Crystallographic data for *trans*-(N,P)-[Pd_2Br_2(μ-C_5H_4N-C^2,N)$_2$(μ-dppb)]·MeCN **5** and *cis*-[PdBr(η^1-C_5H_4NH-C^2)(η^2-dppf)]Br·0.5MeOH **6**

	5·MeCN	**6**·0.5MeOH
Chemical formula	$C_{38}H_{36}Br_2N_2P_2Pd_2$·MeCN	$C_{39}H_{33}Br_2FeNP_2Pd$·0.5MeOH
M	996.30	908.68
Colour and habit	Light yellow block	Brownish red block
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.4392(2)	9.7095(1)
b/Å	12.6975(2)	10.6396(1)
c/Å	16.8905(3)	18.9842(1)
α/°	70.198(1)	89.378(1)
β/°	75.766(1)	85.003(1)
γ/°	73.886(1)	67.925(1)
U/Å^3	1994.96(6)	1809.98(3)
Z	2	2
F(000)	984	902
D_c/g cm^{-3}	1.659	1.667
R_{int}	0.0201	0.0256
μ/mm^{-1}	3.016	3.224
Reflections collected	12548	12093
Independent reflections	8929	8582
Observed reflections, n	7322	7000
Residual electron densities/e Å^{-3}	+0.770 to −0.844	+1.092 to −1.151
R	0.0394	0.0395
R'	0.0956	0.1060
Goodness of fit, S	1.042	1.036

the electron density fluctuated in the range 1.092 to −1.151 e Å^{-3}. The top four peaks were associated with Pd(1). There was no shift in the final cycles. Although we were not able to locate the pyridinium proton directly, all the data are more consistent with a C- rather than an N-bonded model. The former gives a lower R and R' factors. The difference in the isotopic thermal parameters between the atoms in question is less in the C-bonded model. The residual electron density in the N-bonded case also vanishes in the C-bonded model. Further crystallographic details are given in Table 2.

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