Synthesis of a Bis(NHC)Pd Complex *via* oxidative addition of a C-C bond in a biimidazolium ion.

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Supporting Information

General Information

All solvents were dried and degassed before use: AR grade DMSO and DMF were stored over 4Å molecular sieves and dichloromethane was stirred with $CaCl_2$ then distilled from P_2O_5. DMSO, DMF and dichloromethane were degassed by at least three freeze-pump-thaw cycles. Methanol was distilled from Mg and degassed by bubbling nitrogen gas through the solvent for 20 mins. ^{1}H NMR spectra were recorded on either a Bruker ARX300 (300.13 MHz for ^{1}H, 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P) Bruker AV-500 MHz (500.13 MHz for ^{1}H, 125.77 MHz for ^{13}C and 202.46 MHz for ^{31}P) or Bruker AV-600 MHz (600.13 MHz for ^{1}H, 150.90 MHz for ^{13}C and 242.94 MHz for ^{31}P) spectrometers at 298 K unless otherwise specified. [1]H and ^{13}C chemical shifts were referenced to internal solvent resonances[1] and ^{31}P chemical shifts were referenced to an external 85 % H_3PO_4 solution.

Electrochemical experiments were performed on an eDAQ e-corder 401 potentiostat with a platinum working electrode at 200 mVs[-1], using a 0.1 M Bu_4NClO_4 supporting electrolyte and a silver/silver chloride reference electrode. UV-Vis spectra were recorded on a Perkin Elmar Lambda 25 spectrophotometer. Mass spectra were obtained using a VG Autospec Mass Spectrometer using electrospray ionisation (low resolution) or fast atom bombardment (FAB, high resolution) with a cesium ion source and a *m*-nitrobenzyl alcohol matrix. Microanalyses were performed by the Microanalytical Laboratory at the Research School of Chemistry, Australian National University, Canberra, Australia.

All procedures were carried out in an inert atmosphere using standard Shlenk techniques or in a nitrogen-filled glove-box. Palladium acetate (Precious Metals Online), sodium tetraphenylborate, methyl iodide (Ajax), α,α'-dibromo-*ortho*-xylene (Aldrich) were used as received and triphenyl phosphine was recrystallised from hexanes. 1,1'-Dimethyl-2,2'-biimidazole[2,3] and 1,1'-(α,α'-*o*-xylylene)-2,2'-biimidazole[3] were prepared by methods based on literature procedures.

*Synthesis and characterization of **3**.2Br*
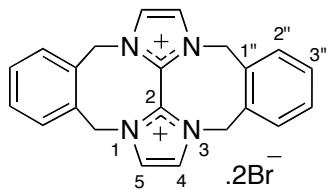
A solution of 1,1'-(α,α'-*o*-xylylene)-2,2'-biimidazole (464 mg, 1.97 mmol) and α,α'-dibromo-*ortho*-xylene (519 mg, 1.97 mmol) in DMF (5 mL) was stirred at 105 ˚C for 18 h. A precipitate formed within 15 mins. The mixture was cooled, dichloromethane (ca. 10 mL) was added and the resulting hygroscopic white solid was collected and recrystallised from ethanol/water yielding pale yellow crystals (618 mg, 63 %).

Anal. Calcd for $C_{22}H_{20}N_4Br_2.0.5H_2O$: C, 51.89; H, 4.16; N, 11.00. Found: C, 51.72; H, 4.23; N, 10.79.

^{1}H NMR (500.13 MHz, d_6-DMSO) δ: 5.85 (AB pattern, 8H, 4 x CH$_2$), 7.54 (m, 4H, 4 x ArH2"), 7.62 (m, 4H, 4 x ArH3"), 8.50 (s, 4H, H4, H4', H5 and H5').

^{13}C NMR (125.77 MHz, d_6-DMSO) δ: 52.62 (*C*H$_2$), 127.66 (C4/5), 129.62 (2 x C2), 129.71 (4 x C2"), 130.96 (4 x ArC1"), 131.24 (4 x C3").

Mass Spectrum (EI): *m/z* 419.087022 ($C_{22}H_{20}N_4Br$ requires 419.087133).

Crystals suitable for X-ray crystallographic studies were grown by diffusion of vapours between acetone and a solution of the salt in methanol.

*Synthesis and characterization of **2**.BPh₄*
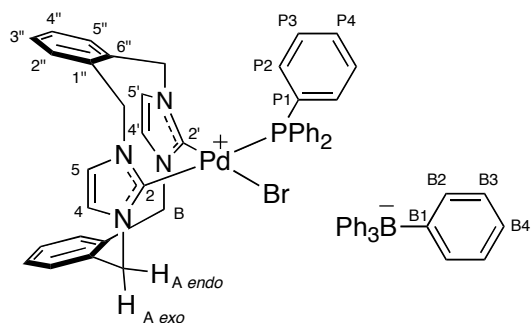
A mixture of **3**.2Br (102 mg, 0.2 mmol), palladium acetate (46 mg, 0.2 mmol), triphenylphosphine (160 mg, 0.61 mmol) and water (4 μL, 0.22 mmol) in dry DMSO (ca 8 mL) was stirred at 90 ˚C for 15 hours. The solution was cooled, the solvent removed under vacuum (ca 50 ˚C) and the residue was extracted with methanol (ca. 6 mL). A solution of sodium tetraphenylborate (103 mg, 0.3 mmol) in methanol (ca. 2 mL) was added and the resulting mixture was stirred at room temperature for 10 mins. The solid was collected, washed with methanol and recrystallised by layering a concentrated solution of the complex in dichloromethane with methanol to yield pale orange crystals (110 mg, 50 %).

Anal. Calcd for $C_{64}H_{55}N_4BPBrPd.1.5CH_2Cl_2.CH_3OH$ C, 63.01; H, 4.93; N, 4.42. Found: C, 63.09; H, 4.78; N, 4.51.

^{1}H NMR (600.13 MHz, d_6-DMSO) δ: 4.57 (d, 2H, J = 14 Hz, H_B endo or exo), 5.24 (d, 2H, J = 14 Hz, H_A endo or exo), 5.98 (d, 2H, J = 14 Hz, H_B endo or exo), 6.33 (d, 2H, J = 14 Hz, H_A endo or exo), 6.79 (d, 4H, J = 7.2 Hz, 4 x H_{B4}), 6.92 (t 8H, J = 7.4 Hz, 8 x H_{B3}), 7.18 (m, 10H, 8 x H_{B2} and H4' and H5'), 7.36 (dt, 2H, J = 1.4 and 7.5 Hz, H5"), 7.40 (dt, 2H, J = 1.4 and 7.5 Hz, H2"), 7.52 (d, 2H, $^4J_{H-P}$ = 1.2 Hz, H4 and H5), 7.53 (m, 6H, 6 x H_{P3}), 7.59 (dt, 3H, J = 1.7 and 7.4 Hz, H_{P4}), 7.67 (m, 8H, 2 x H4" and 6 x H_{P2}), 7.83 (dt, 2H, J = 1.1 and 7.5 Hz, 2 x H3").

^{13}C NMR (150.90 MHz, d_6-DMSO) δ: 50.5 (C_B), 50.8 (C_A), 121.9 (C_{B4}), 122.4 (d, $^4J_{C-P}$ = 5 Hz, C4 and C5), 122.7 (C4' and C5'), 125.3 (q, $^2J_{C-B}$ = 2.7 Hz, C_{B3}), 129.0 (d, $^3J_{C-P}$ = 10 Hz, C_{P3}), 129.53 (d, $^1J_{C-P}$ = 45 Hz, C_{P1}), 129.56 (C2" or C5"), 129.7 (C2" or C5"), 131.1 (C_{P4}), 132.15 (C3" or C4"), 132.27 (C3" or C4"), 133.8 (d, $^2J_{C-P}$ = 12 Hz, C_{P2}), 134.9 (C1"), 135.51 (C_{B2}), 135.58 (C6"), 159.5 (C2', $^2J_{C-P}$ = 8.5 Hz), 163.28 (C2, $^2J_{C-P}$ = 160 Hz), 163.30 (q, $^1J_{C-B}$ = 49.3 Hz, C_{B1}).

^{31}P NMR (121.5 MHz, d_6-DMSO) δ: 19.44.

Mass Spectrum (FAB) *m/z* 787.081818 ($C_{40}H_{35}N_4P^{79}Br^{106}Pd$ requires 787.081747), 789.081645 ($C_{40}H_{35}N_4P^{81}Br^{106}Pd$ requires 789.079701), 791.079384 ($C_{40}H_{35}N_4P^{81}Br^{108}Pd$ requires 791.080120)

Synthesis and characterization of 4.2I
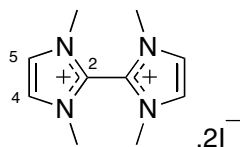
A solution of 1,1'-dimethyl-2,2'-biimidazole (150 mg, 0.93 mmol) and methyliodide (0.5 mL, 8.0 mmol) in dmf (3 mL) was stirred at 70 °C for 17 h in a thick-walled flask fitted with a Young's tap. Dichloromethane (c.a. 10 mL) was added and the resulting pale yellow powder was collected, washed with dichloromethane and diethylether and dried *in vacuo* (331 mg, 80 %).
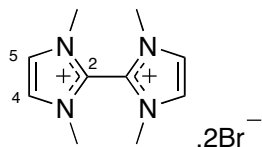
Anal. Calcd for $C_{10}H_{16}N_4I_2$ C,26.93; H, 3.62; N, 12.56. Found C, 27.12; H, 3.77; N, 12.48.

^{1}H NMR (300.13 MHz, d_6-DMSO) δ: 3.88 (s, 4 x CH$_3$), 8.34 (s, 4H, 2 x H4 and 2 x H5).

^{13}C NMR (75.5 MHz, d_6-DMSO) δ: 36.59 (4 x CH$_3$), 124.77 (C2/2'), 128.03 (C4 and C5).

Mass Spectrum (FAB): *m/z* 192.137925 ($C_{10}H_{16}N_4I$ requires 192.137497).

Synthesis and characterization of 4.2Br

A solution of potassium hexafluorophosphate (108 mg, 0.59 mmol) in water (ca 2 mL) was added to a stirred solution of **4**.2I (61 mg, 0.14 mmol) in water (ca 1 mL) and the resulting mixture was stirred at room temperature for 20 mins. The resulting precipitate was collected, washed with water (ca 2 mL) and air dried for 2 hours to afford **4**.2PF$_6$ as a white powder (41 mg, 70 %). **4**.2PF$_6$ (38 mg, 0.09 mmol) was dissolved in dry acetone (ca 1 mL), a solution of tetrabutylammonium bromide (122 mg, 0.38 mmol) in acetone (1 mL) was added and the resulting mixture was stirred at room temperature for 30 mins. The precipitate was collected, washed with acetone (1 ml) and dried under vacuum to give **4**.2Br as pale yellow powder (18 mg, 68%).

^{1}H nmr (600.13 MHz, d_6-DMSO) δ: 3.88 (s, 12H, 4 x CH$_3$), 8.30 (s, 4H, 4 x CH).

^{13}C nmr (150.90 MHz, d_6-DMSO) δ: 36.50 (4 x CH$_3$), 124.75 (2 x C2), 127.99 (4 x CH).
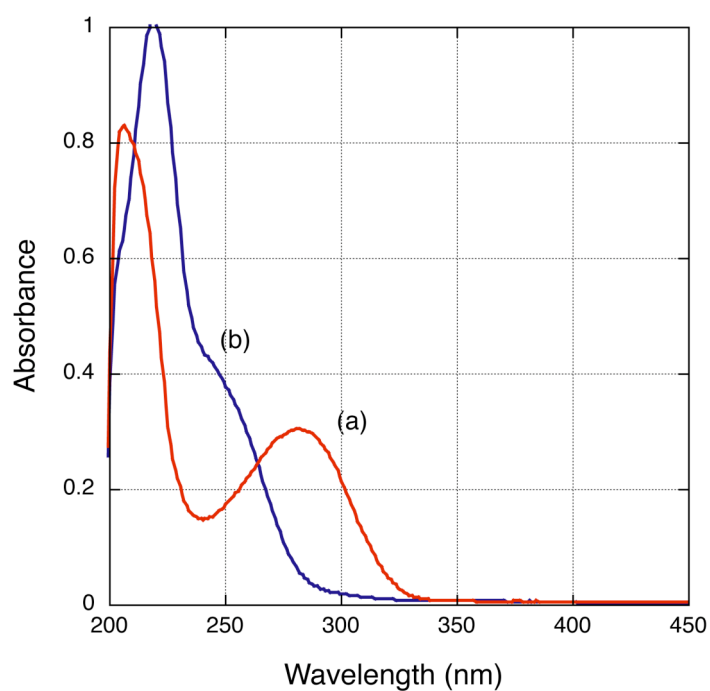
Figure S1. UV/vis absorbance spectra of ethanolic solutions of:

      (a) **3**.2Br (3.3 x 10^{-5} M); and
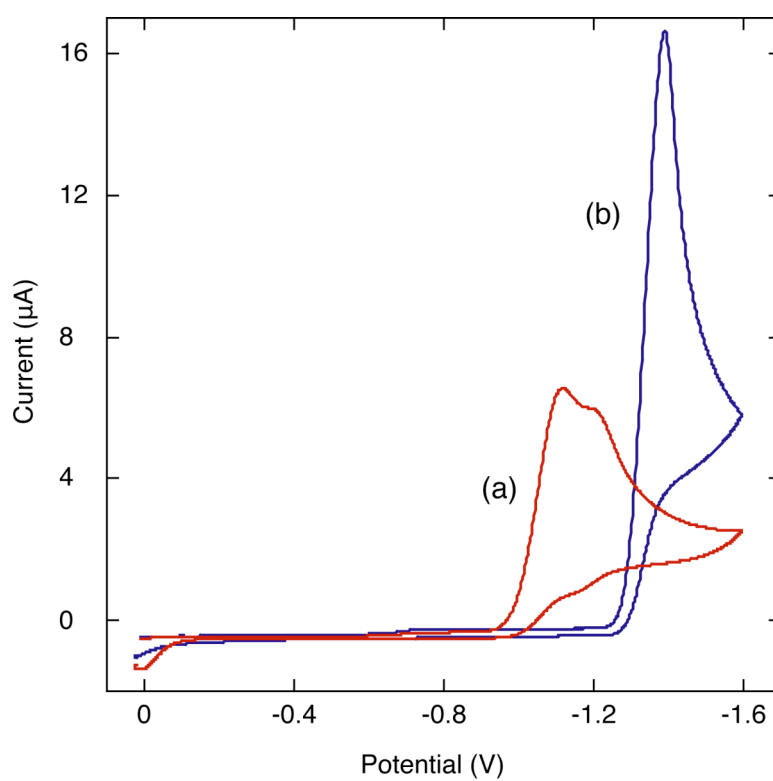
      (b) **4**.2I (5.3 x 10^{-5} M).

Figure S2. Cyclic voltamograms of (a) **3**.2Br and (b) **4**.2I. Electrolyte, 0.1 M Bu_4NClO_4 in DMSO; Scan rate 200 mVs^{-1}; Pt working electrode and Ag/AgCl reference electrode.

Structure determinations

Full spheres of CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans; monochromatic Mo Kα radiation; $\lambda = 0.7107_3$ Å; *T ca.* 153 K) yielding $N_{t(otal)}$ reflections, these merging to N unique after 'empirical/multiscan' absorption correction, (proprietary software), N_o with $F > 4\sigma(F)$ being considered 'observed'. All data were employed in the full matrix least squares refinements on F^2 (weights $(\sigma^2(F^2) + n_wF^2)^{-1}$, refining anisotropic displacement parameters for the non-hydrogen atoms, hydrogen atoms being included, constrained at estimates. Neutral atom complex scattering factors were employed within the Xtal 3.7 system.[4] Pertinent results are given below and in the associated Table and Figures (the latter showing non-hydrogen atoms with 50% probability amplitude displacement ellipsoids, hydrogen atoms having arbitrary radii of 0.1 Å), and the associated .cif files (excluding structure factor amplitudes).

Crystal/refinement data

2.BPh$_4$.1.80CH$_2$Cl$_2$ $\equiv$ C$_{65.8}$H$_{58.6}$BBrCl$_{3.6}$N$_4$PPd, M = 1261.1. Orthorhombic, space group *Fdd*2 $(C_{2v}^{19}$, No. 43$)$, $a = 38.434(2)$, $b = 48.007(3)$, $c = 12.7080(7)$ Å, $V = 23448$ Å^3. D_c ($Z = 16$) = 1.43$_2$ g cm^{-3}. $\mu_{Mo} = 1.24$ mm^{-1}; specimen: 0.48 x 0.42 x 0.36 mm; 'T'$_{min/max}$ = 0.91. $2\theta_{max} = 68°$; $N_t = 86281$, $N = 22236$ ($R_{int} = 0.034$), $N_o = 19090$; $R1 = 0.037$, $wR2 = 0.034$ ($n_w = 0.04$); gof = 1.05; $|\Delta\rho_{max}|$ = 0.77 e Å^{-3}. $x_{abs} = -0.012(4)$).

Variata. Solvent residues were modelled in terms of one molecule of CH$_2$Cl$_2$, full site occupancy, and a second with site occupancy refining to 0.801(3).

3.2Br.Me$_2$CO $\equiv$ C$_{25}$H$_{26}$Br$_2$N$_4$O, M = 558.3. Triclinic, space group $P\bar{1}$ $(C_i^1$, No. 2$)$, $a = 9.969(1)$, $b = 10.286(1)$, $c = 11.985(1)$ Å, $\alpha = 80.957(3)$, $\beta = 86.821(3)$, $\gamma = 75.278(3)°$, $V = 1174$ Å^3. D_c ($Z = 2$) = 1.58$_0$ g cm^{-3}. $\mu_{Mo} = 3.5$ mm^{-1}; specimen: = 0.32 x 0.22 x 0.15 mm; 'T'$_{min/max}$ = 0.70. $2\theta_{max} = 70°$; $N_t = 20857$, $N = 10267$ ($R_{int} = 0.038$), $N_o = 6546$; $R1 = 0.045$, $wR2 = 0.114$ ($n_w = 0.6$); gof = 1.038; $|\Delta\rho_{max}|$ = 1.7(3) e Å^{-3}.

Variata. The solvate molecule was nicely ordered and refined unproblematically. There is a large number of Br… ligand hydrogen contacts < 3.1 Å: for Br(1) six lie in the range 2.76 - 3.02 Å, and for Br(2) five in the range 2.79 - 2.97 Å. There are intermolecular solvent O…H contacts at 2.5$_2$ Å.

4.2I. $\equiv C_{10}H_{16}I_2N_4$, $M = 446.1$. Monoclinic, space group $P2_1/c$ $(C_{2h}^5$, No. 14$)$, $a = 9.2022(5)$, $b = 15.0503(8)$, $c = 11.0279(6)$ Å, $\beta = 104.603(1)°$, $V = 1478$ Å^3. D_c $(Z = 4) = 2.00_4$ g cm^{-3}. $\mu_{Mo} = 4.2$ mm^{-1}; specimen: $= 0.38$ x 0.18 x 0.18 mm; $'T'_{min/max} = 0.63$. $2\theta_{max} = 75°$; $N_t = 29258$, $N = 7750$ $(R_{int} = 0.026)$, $N_o = 6948$; $R1 = 0.025$, $wR2 = 0.062$ $(n_w = 0.7)$; gof $= 1.046$; $|\Delta\rho_{max}| = 1.4(1)$ e Å^{-3}.

Variata. There are numerous I…H contacts < 3.3 Å, but for each iodine a pair are found to be < 3Å: for I(1)...H(11c),H(11a)(1+x, ½-y, z+½) 2.94 Å (x2) and for I(2))…H(11b), H(13c)(1-x, y-½, 1½ -z) 2.9_5, 2.9_9 Å.
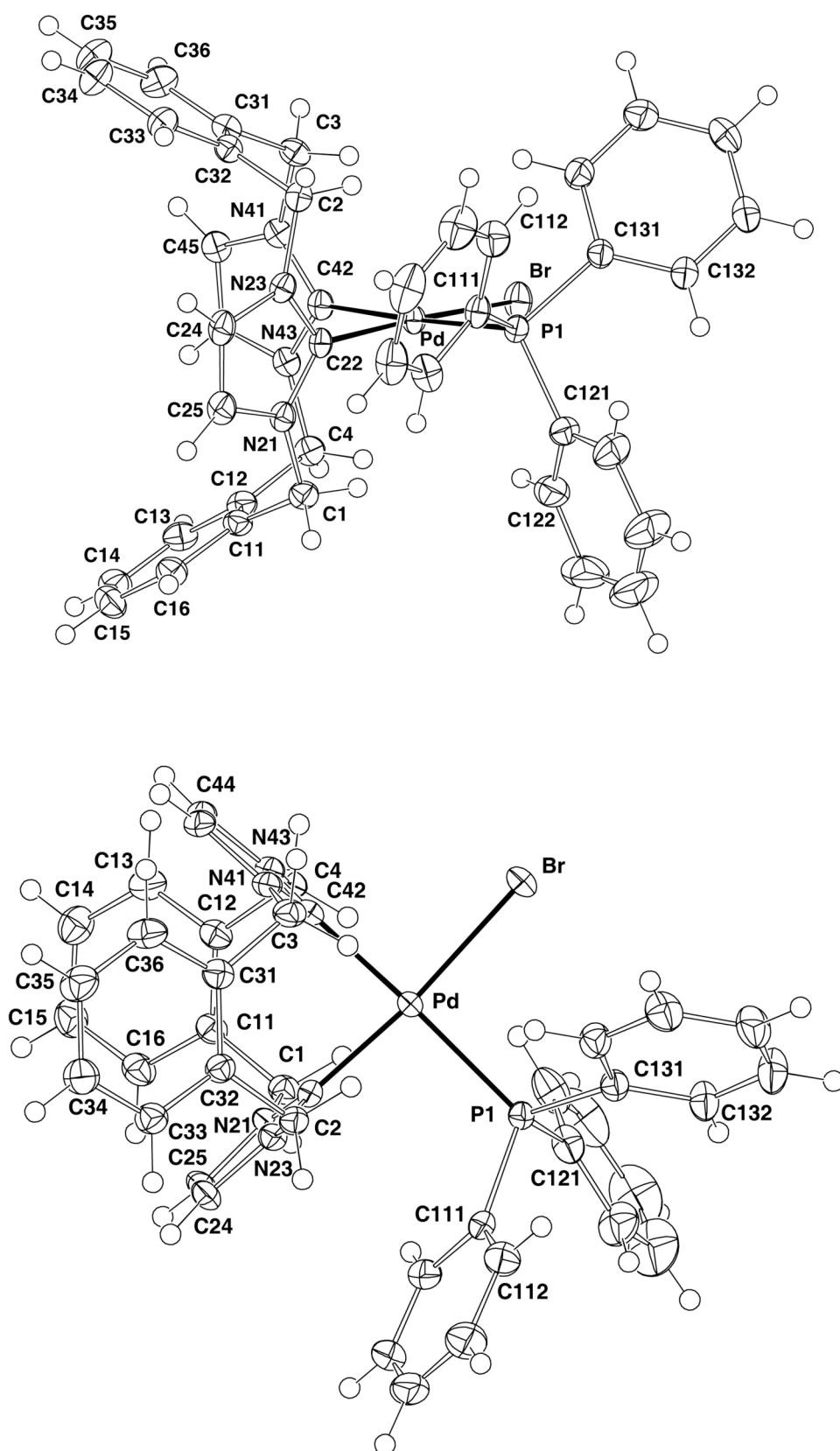
Figure S3. Projections of the cation of **2**. Pd-Br, -P1, -C(22), -C(42) are 2.4610(4), 2.3380(10), 1.999(3), 2.022(4) Å.
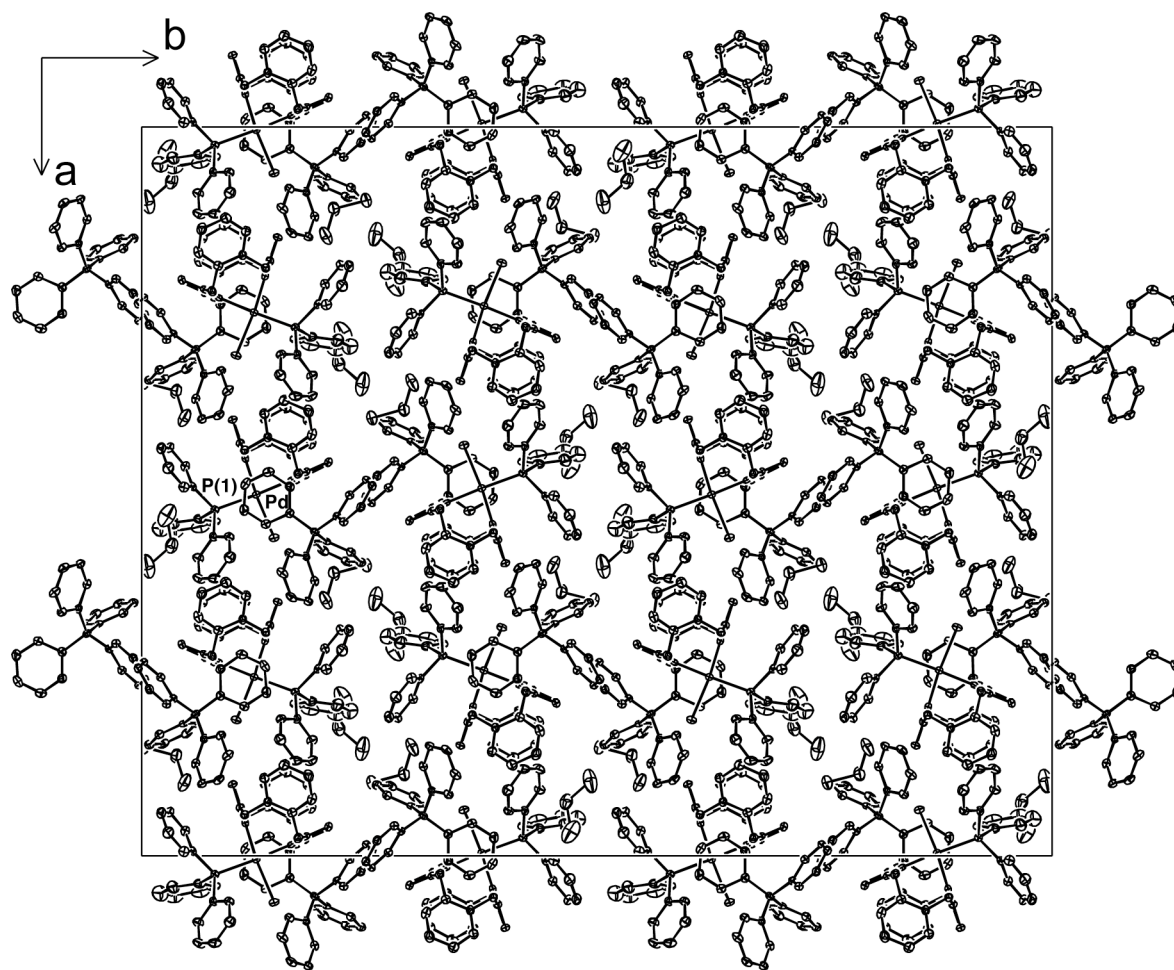
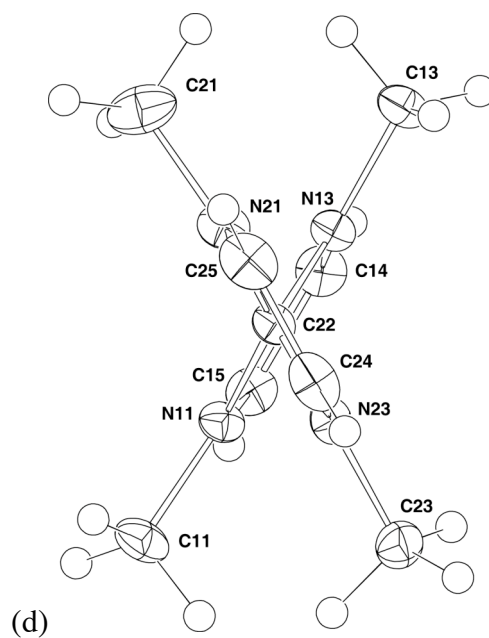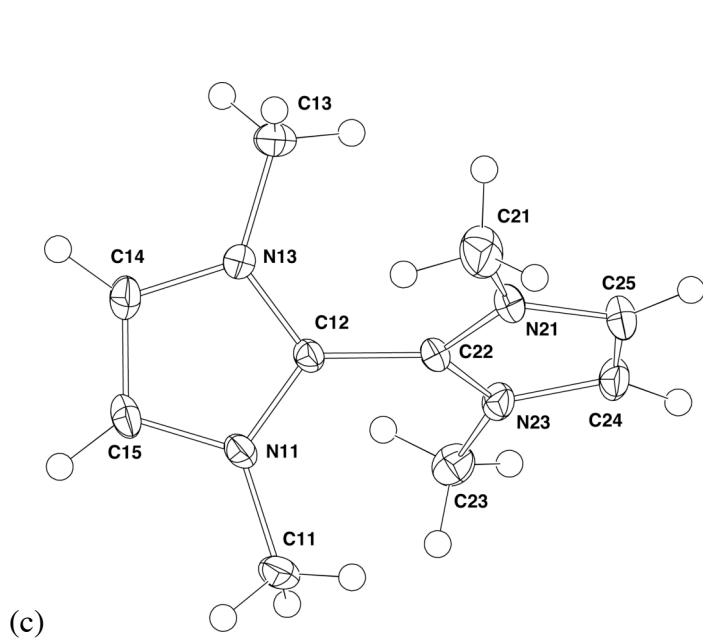**Figure S4.** Unit cell contents of **2.** BPh$_4$. 1.8CH$_2$Cl$_2$ projected down *c*.
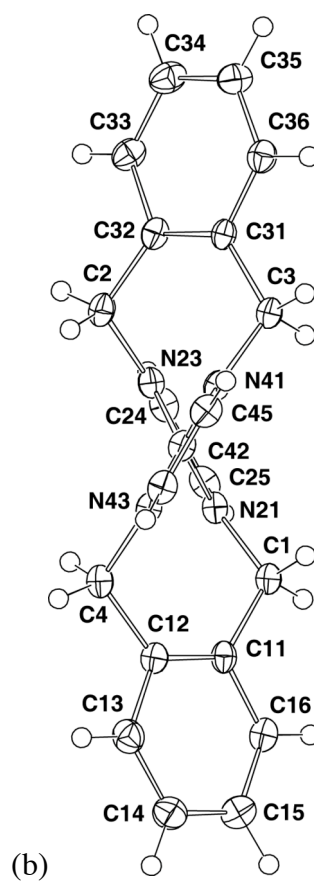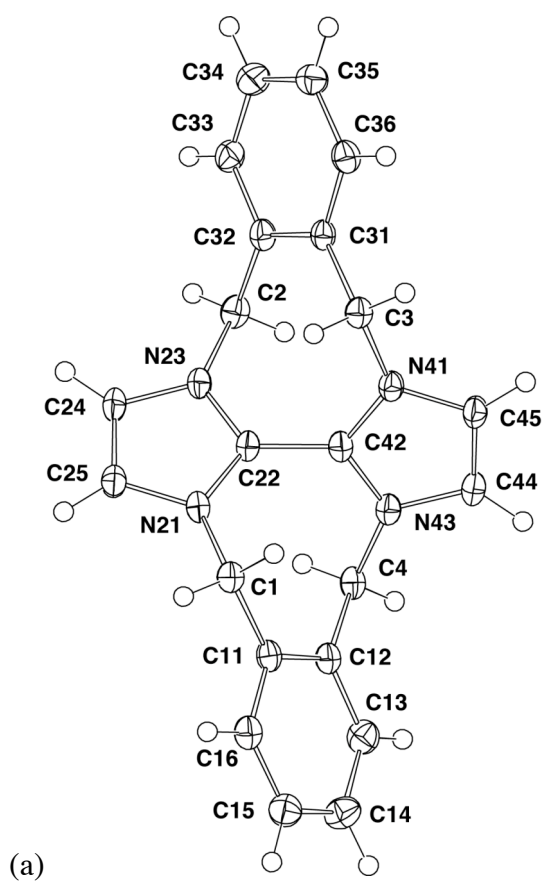
Figure S5. Projections of the single cations of **3** [(a) and (b)] and **4** [(c) and (d)].

(a)

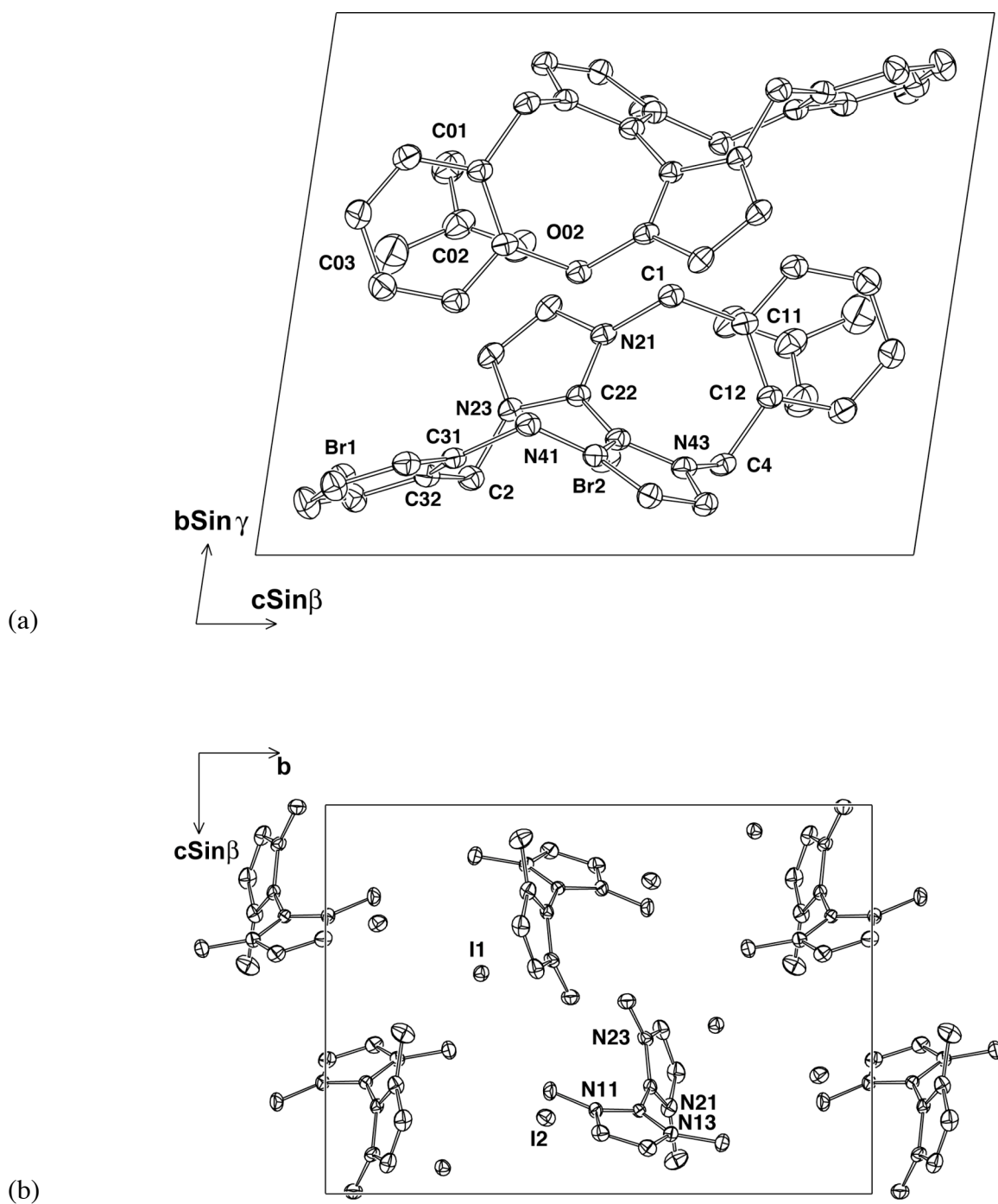
(b)

Figure S6. Unit cell contents of (a) **3**. 2Br. Me$_2$CO and (b) **4**. 2I, both projected down *a*.
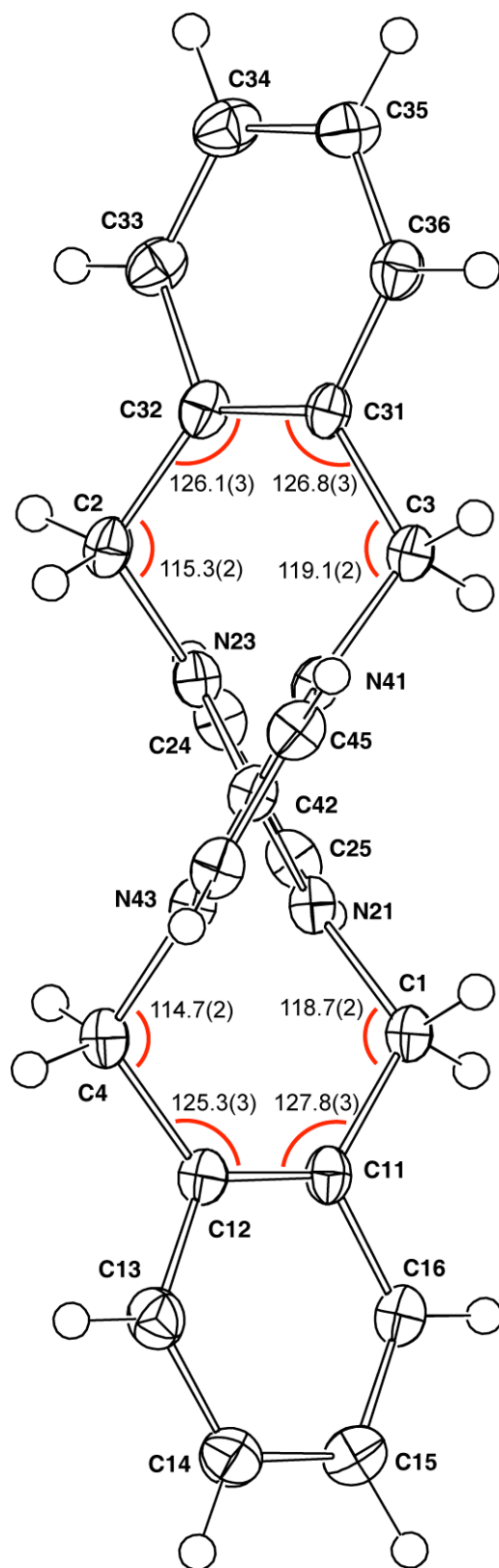
Figure S7. Projection of the cation **3**, showing selected C-C-C angles suggestive of strain within the bridging groups.

Table S1. Selected 'ligand' geometries

C(x) are exocyclic pendant atoms from the imidazole ring nitrogen

Compound/ring(n)	**2** (2,4)	**3** (2,4)	**4** (1,2)
Distances (Å)			
C(n2)-C(n'2)(/Pd)	1.999(3), 2.022(4)	1.439(4)	1.453(3)
N(n1)-C(n2)	1.344(6), 1.364(6)	1.330(4), 1.334(4)	1.345(3), 1.339(3)
C(n2)-N(n3)	1.341(6), 1.315(6)	1.328(4), 1.325(4)	1.341(3), 1.335(3)
N(n1)-C(n5)	1.396(5), 1.378(5)	1.376(4), 1.371(4)	1.375(3), 1.374(4)
N(n3)-C(n4)	1.384(6), 1.388(5)	1.373(4), 1.373(4)	1.372(3), 1.375(3)
C(n4)-C(n5)	1.326(7), 1.320(6)	1.359(4), 1.364(4)	1.361(3), 1.347(3)
Angles (degrees)			
(Pd/)C(n2')-C(n2)-N(n1)	126.6(3), 125.2(3)	125.2(3), 125.8(2)	125.9(2), 126.6(2)
(Pd/)C(n2')-C(n2)-N(n3)	126.9(3), 129.3(3)	124.6(3), 124.3(3)	126.0(2), 125.6(2)
N(n1)-C(n2)-N(n3)	106.5(3), 105.5(3)	110.2(2), 109.9(3)	108.0(2), 107.8(2)
C(n2)-N(n1)-C(n5)	109.0(4), 109.4(4)	107.2(2), 107.6(2)	108.7(2), 108.8(3)
C(n2)-N(n3)-C(n4)	109.8(4), 111.0(3)	107.9(3), 108.0(3)	109.8(2), 108.2(2)
C(n2)-N(n1)-C(x)	125.1(3), 124.9(3)	124.0(2), 123.8(2)	126.9(2), 126.5(2)
C(n5)-N(n1)-C(x)	125.8(4), 125.6(3)	127.5(3), 127.9(2)	124.4(2), 124.3(2)
C(n2)-N(n3)-C(x)	124.7(3), 124.9(3)	123.0(2), 123.8(2)	127.1(2), 126.9(2)
C(n4)-N(n3)-C(x)	125.3(4), 124.0(3)	128.6(2), 128.0(2)	123.9(2), 124.9(1)
N(n1)-C(n5)-C(n4)	107.4(4), 107.4(4)	107.7(3), 107.4(3)	107.2(2), 107.5(2)
N(n3)-C(n4)-C(n5)	107.2(4), 106.7(4)	107.0(3), 107.0(2)	107.2(2), 107.7(2)
Interplanar dihedral angles (degrees)			
C3N2/C3N2	83.6(2)	56.2(1)	59.14(9)
C6/C6	62.2(2)	80.7(1)	
C6(1)/C3N2(2)	64.1(2)	49.4(1)	
C6(1)/C3N2(4)	75.1(2)	61.9(1)	
C6(3)/C3N2(2)	72.7(2)	58.8(1)	
C6(3)/C3N2(4)	67.4(2)	50.1(1)	

Phosphine torsion angles (degrees): Pd-P(1)-C(n11)-C(n12/6) 70.5(2), 12.5(2), 38.7(2)°.

Table S2. Close interspecies halide…hydrogen contact distances (Å) (est.)

Atoms	Distance		Atoms	Distance
(a) **2**.BPh$_4$.1.80CH$_2$Cl$_2$ (Br…H < 3 Å)				
Br…H(245[i])	2.99		Br…H(01A)	2.97
Transformation of the asymmetric unit:	i	x, y, 1+z		
(b) **3**.2Br.Me$_2$CO (Br…H < 3 Å)				
Br(1)…H(14i)	2.99		Br(2)…H(2b[iv])	2.79
…H(15)[ii]	2.91		…H(4a)	2.80
…H(2a)	2.72		…H(45)	2.95
…H(34[iii])	2.90		…H(1a[ii])	2.83
…H(4b[iv])	2.76		…H(3a[v])	2.97
…H(44[ii])	3.01			
Transformations of the asymmetric unit:	i	x, y, z-1	ii	1-x, 1-y, 1-z
iii	1-z, $\bar{y}$, $\bar{z}$	iv	1-x, $\bar{y}$, 1-$\bar{z}$	v	x+1, y, z
(c) **4**.2I (I…H < 3Å)				
I(1)…H(11a[i])	2.94		I(2)…H(11b)	2.95
…H(11c)	2.94		…H(13c[ii])	2.99
Transformations of the asymmetric unit:	i	x, ½-y, z-½	ii	1-x, y-½, 1½-z

References

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(2) Melloni, P.; Dradi, E.; Logemann, W.; de Carneri, I.; Trane, F. *J. Med. Chem.* **1972**, *15*, 926-930.

(3) Thummel, R. P.; Goulle, V.; Chen, B. *J. Org. Chem.* **1989**, *54*, 3057-3061.

(4) Hall, S. R.; du Boulay, D. J.; Olthof-Hazekamp (eds.), R. *The Xtal 3.7 System*; The University of Western Australia: Perth, 2001.