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Synthetic and structural studies of methyl- and phenylpalladium(II) complexes of poly(pyrazol-1-yl)borates, and the η^3-allylpalladium(II) complex Pd(η^3-C_3H_5){$(pz)_3BH$-N,N'}

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Abstract

The poly(pyrazol-1-yl)borate complexes PdMe{$(pz)_3BR$-N,N'}(PPh_3) (R = H, pz) are formed on the reaction of [PdMe(SMe_2)(μ-I)]$_2$ with K[$(pz)_3BR$] in the presence of PPh_3 and $TlPF_6$, and the phenylpalladium(II) analogues are formed directly from PdIPh(tmeda) (tmeda = N,N,N',N'-tetramethylethylenediamine) and K[$(pz)_3BR$] in the presence of PPh_3. X-ray diffraction studies of PdR{$(pz)_4B$-N,N'}(PPh_3) (R = Me, Ph) and PdPh{$(pz)_3BH$-N,N'}(PPh_3) reveal square planar geometry for palladium with the poly(pyrazol-1-yl)borate ligands in bidentate mode. The structure of Pd(η^3-C_3H_5){$(pz)_3BH$-N,N'} has also been determined, and it contains a bidentate tris(pyrazol-1-yl)borate group with the η^3-allyl group forming a dihedral angle of 125.5(2.1)° with the PdN_2 plane. In both PdPh{$(pz)_3BH$-N,N'}(PPh_3) and Pd(η^3-C_3H_5){$(pz)_3BH$-N,N'} the uncoordinated pyrazole group lies above the coordination plane.

Keywords: Palladium; Poly(pyrazol-l-yl)borates; Allyl; Crystal structure

1. Introduction

An extensive organopalladium chemistry of poly (pyrazol-1-yl)borate ligands $[(pz)_nBR_{4-n}]^-$ has been developed [1,2], but synthetic studies have not been reported for simple methylpalladium(II) and phenylpalladium(II) species, and structural studies are restricted to Pd{2-(NMe_2CH_2)$C_{10}H_6$-C,N}{$(pz)_3BH$-N,N'}.1/2MeOH [3], palladium(IV) complexes $PdMe_3${$(pz)_3BR$-N,N',N''} (R = H, pz) [2,4], and the η^3-allylpalladium(II) complex {Pd(η^3-C_3H_5)$_2$}$_2${$(pz)_3B$-$B(pz)_3$-N,N,N',N'} [5]. In developing oxidation state +IV organopalladium chemistry [6] we have found that some of the most stable complexes are those containing tris(pyrazol-1-yl)borate as a supporting ligand [4,7], and that use of these ligands coordinated to $Pd^{II}Me_2$ and $Pd^{II}MePh$ substrates has allowed the first observation of oxidation of palladium(II) to palladium(IV) by water in unusual reactions involving both oxidation and methyl group transfer to form $Pd^{IV}Me_3$ and $Pd^{II}R$ (R = Me, Ph respectively) products [4]. As part of a programme aimed at further developing aspects of poly(pyrazol-1-yl)borate chemistry of palladium relevant to these reactions, we report here the synthesis of the fundamental complexes PdR{$(pz)_3BR'$-N,N'}(PPh_3) (R = Me, Ph; R' = H, pz) and structural studies of three of the complexes together with Pd(η^3-C_3H_5){$(pz)_3BH$-N,N'}.

2. Experimental details

The reagents [PdMe(SMe_2)(μ-I)]$_2$ [8] and PdIPh (tmeda) [9] were prepared as previously described, and the synthesis of Pd(η^3-C_3H_5){$(pz)_3BH$} has been reported [1]. NMR spectra were recorded with a Bruker AM 300 spectrometer, and chemical shifts are given in ppm relative to Me_4Si.

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2.1. Synthesis of PdMe{(pz)$_3$BH}(PPh$_3$) (1) and PdMe{(pz)$_4$B}(PPh$_3$) (2)

A solution of [PdMe(SMe$_2$)(μ-I)]$_2$ (0.03 g, 0.05 mmol) and K[(pz)$_3$BH] (0.024 g, 0.10 mmol) in tetrahydrofuran (15 ml) was treated with TlPF$_6$ (0.035 g, 0.10 mmol). A yellow solid was formed immediately. The mixture was stirred for 15 min, PPh$_3$ (0.025 g, 0.10 mmol) added, and after further stirring for 2–3 h the solvent was removed under vacuum. The residue was extracted with acetone (2 × 3 ml) and added to water (10 ml) to give a fine white suspension. The solid was collected after centrifugation and vacuum dried (0.056 g, 95%). Anal. Found: C, 55.9; H, 4.7; N, 13.6, $C_{28}H_{28}BN_6PPd$ Calc.: C, 56.3; H, 4.7; N, 14.1%. ^{1}H NMR (CDCl$_3$): δ 7.34–7.45 (15H, m, Ph), 7.64 (3H, d, H(3 or 5), $^3J = 2.1$ Hz), 7.18 (3H, s(br), H(3 or 5)), 6.11 (3H, 't', H(4)), 0.41 (3H, d, PdMe, $^3J_{(HP)} = 3$ Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 141 (C(3 or 5)), 136.3 (p-Ph), 135 (d, m-Ph), 131.2 (C(3 or 5)), 129 (d, o-Ph), 105.5 (C(4)), 2.7 (br, PdMe).

Complex (2) was obtained analogously (89%). Anal. Found: C, 56.0; H, 4.7; N, 16.0, $C_{31}H_{30}BN_8PPd$ Calc.: C, 56.2; H, 4.6; N, 16.3%. ^{1}H NMR (CDCl$_3$): δ 7.7 (4H, s(b), H(3 or 5)), 7.3–7.5 (15H, m, Ph), 7.1 (2H, s(br), H(3 or 5)), 6.3 (4H, s(br), H(4)), 0.33 (3H, d, PdMe, $^3J_{(HP)} = 3.3$ Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 141.9 (C(3 or 5)), 135.9 (p-Ph), 135 (d, m-Ph), 131 (C(3 or 5)), 128.9 (d, o-Ph), 105.6 (C(4)), 2.4 (d, $^2J_{(P\text{-}C)} = 7.5$ Hz, PdMe).

2.2. Synthesis of PdPh{(pz)$_3$BH}(PPh$_3$) (3) and PdPh{(pz)$_4$B}(PPh$_3$) (4)

A solution of PdIPh(tmeda) (0.038 g, 0.089 mmol) and K[(pz)$_3$BH] (0.031 g, 0.123 mmol) in acetone (8 ml) was warmed at ca. 50°C for 2 min, and PPh$_3$ (0.023 g, 0.089 mmol) was added. On rotary evaporation to a volume of ~ 2 ml and addition of water (3 ml) a fine white suspension formed. After centrifugation solid (3) was collected, washed with water, and vacuum dried (0.052 g, 82%). Anal. Found: C, 59.9; H, 4.7; N, 12.7, $C_{33}H_{30}BN_6PPd$ Calc.: C, 60.2; H, 4.6; N, 12.8%. ^{1}H NMR (CDCl$_3$): δ 7.7 (3H, d, H(3 or 5)), 7.35–7.15 (15H, m, Ph), 7.07 (s, H(3 or 5)) and 7.07–7.01 (m, PdPh), 6.75–6.69 (m, PdPh), 6.09 (3H, 't', H (4)). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 142.2 (C(3 or 5)), 136.2 (p-Ph), 135 (d, m-Ph), 131.1 (C(3 or 5)), 130.9, 130.2, 128.9 (d, o-Ph), 128.2 (PdPh), 123.7 (PdPh), 105 (C(4)).

Complex (4) was obtained analogously (82%). Anal. Found: C, 59.4; H, 4.4; N, 14.8, $C_{36}H_{32}BN_8PPd$ Calc.: C, 59.7; H, 4.5; N, 15.5%. ^{1}H NMR ((CD$_3$)$_2$CO): δ 7.6 (m(br), H(3 or 5)) and 7.5–7.4 (m(br), Ph), 7.2 (br, H(3

Table 1
Crystal data and refinement parameters for PdMe{(pz)$_4$B}(PPh$_3$) (2), PdPh{(pz)$_3$BH}(PPh$_3$) (3), PdPh{(pz)$_4$B}(PPh$_3$) (4), and Pd(η^3-C$_3$H$_5$){(pz)$_3$BH} (5) [a]

	(2) [b]	(3) [c]	(4)	(5)
Formula	$C_{31}H_{30}BN_8PPd$	$C_{33}H_{30}BN_6PPd$	$C_{36}H_{32}BN_8PPd$	$C_{12}H_{15}BN_6Pd$
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$Pbca$ (No. 61)
a (Å)	14.142(11)	14.394(29)	18.295(5)	17.931(7)
b (Å)	14.912(8)	10.979(11)	8.930(4)	18.351(7)
c (Å)	16.500(23)	9.745(14)	20.919(5)	8.645(4)
β (deg)	119.90(8)	92.83(14)	100.00(2)	
V (Å)	3016(6)	1536(4)	3366(2)	2845(2)
Z	4	2	4	8
Mol. wt.	662.8	658.8	724.9	360.5
$D_{calc.}$ (g cm^{-3})	1.46	1.42	1.43	1.68
Crystal size (mm^3)	0.18 × 0.29 × 0.29	0.28 × 0.23 × 0.04	0.26 × 0.58 × 0.24	0.19 × 0.35 × 0.51
μ (cm^{-1})	6.2	6.9	3.8	13.0
F(000)	1352	672	1480	1440
$2\theta_{max}$ (deg)	50	50	60	60
$A^*_{min,max}$	1.09, 1.17	1.03, 1.17	1.14, 1.21	1.27, 1.51
N	5110	4256	9600	6243
N_0	3540	2712	6355	1949
R	0.052	0.052	0.038	0.063
R_w	0.055	0.052	0.039	0.065

[a] For all of the complexes assignment of uncoordinated ring nitrogen atoms was made on the basis of refinement behaviour and associated difference map residues indicative of associated hydrogen atoms.

[b] The methyl substituent upon refinement yielded an unrealistic very small thermal tensor; examination of a difference map showed an artefact more distant from the metal, and, having regard to the method of synthesis of the complex, a fractional iodine was disposed thus and successfully refined, population of the iodine and methyl not being inconsistent with a totality of unity. The latter constraint was applied and the model refined meaningfully, with site occupancies converging to $x_C = 0.945(2)$, $1 - x_C = x_I = 1 - 0.945(2)$, and with tolerable geometries and thermal parameter behaviour.

[c] $\alpha = 92.95(10)°$, $\gamma = 90.91(12)°$.

or 5)) and 7.08 (m(br), PdPh), 6.87–6.78 (m, PdPh), 6.47 (br, H(4)). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 142.8 (br, C(3 or 5)), 136.3 (b, *p*-Ph), 135 (d, *m*-Ph), 131 (C(3 or 5)), 130.8, 130.1, 128.9 (d, *o*-Ph), 128.1 (PdPh), 126.1 (PdPh), 123.7 (PdPh), 105.6 (C(4)).

2.3. Crystallography

Complex (**2**) crystallized on slow evaporation of a solution in diethyl ether, complexes (**3**) and (**4**) were obtained similarly from acetone and hexane respectively, and complex (**5**) was recrystallized from 4:1 water/acetone. Samples of complex (**2**) were also examined by X-ray microprobe analysis and simple tests for the presence of iodide using $AgNO_3$. Iodide could not be detected in the sample obtained from the preparation, but single crystals similar to those examined crystallographically were shown by microprobe analysis to contain a small amount of iodide.

Table 2
Non-hydrogen atom coordinates and equivalent isotropic displacement parameters for PdMe{$(pz)_4B$}(PPh_3) (**2**)

Atom	x	y	z	U_{eq} (Å^2)
Pd	0.48654(4)	0.20305(4)	0.20484(3)	0.0354(2)
P(1)	0.3047(1)	0.1987(1)	0.1443(1)	0.0366(8)
C(111)	0.2487(6)	0.3121(4)	0.1233(5)	0.040(3)
C(112)	0.1520(6)	0.3360(5)	0.0430(5)	0.054(4)
C(113)	0.1179(7)	0.4256(7)	0.0296(6)	0.073(5)
C(114)	0.1770(8)	0.4893(6)	0.0952(8)	0.076(6)
C(115)	0.2729(8)	0.4665(5)	0.1738(7)	0.066(5)
C(116)	0.3076(6)	0.3784(5)	0.1873(6)	0.055(4)
C(121)	0.2241(5)	0.1407(5)	0.0314(5)	0.041(3)
C(122)	0.1160(6)	0.1185(5)	0.0005(5)	0.055(4)
C(123)	0.0536(7)	0.0791(6)	−0.0862(6)	0.069(4)
C(124)	0.0978(8)	0.0625(6)	−0.1413(5)	0.070(5)
C(125)	0.2048(7)	0.0817(6)	−0.1110(5)	0.063(5)
C(126)	0.2687(6)	0.1214(5)	−0.0238(5)	0.048(4)
C(131)	0.2584(5)	0.1472(5)	0.2174(4)	0.038(3)
C(132)	0.2423(6)	0.0541(5)	0.2155(5)	0.045(3)
C(133)	0.2131(6)	0.0133(5)	0.2756(5)	0.051(4)
C(134)	0.1994(6)	0.0650(6)	0.3376(5)	0.056(4)
C(135)	0.2143(6)	0.1572(6)	0.3415(5)	0.056(4)
C(136)	0.2462(6)	0.1968(5)	0.2831(5)	0.047(3)
C[a]	0.454(2)	0.282(1)	0.095(1)	0.051(6)
I[a]	0.460(2)	0.304(1)	0.075(1)	0.041(6)
B	0.6925(6)	0.2446(6)	0.4136(5)	0.040(4)
N(11)	0.6348(4)	0.1584(4)	0.4132(4)	0.038(3)
N(12)	0.5432(4)	0.1293(3)	0.3330(4)	0.039(3)
C(13)	0.5135(6)	0.0533(5)	0.3557(5)	0.049(4)
C(14)	0.5811(6)	0.0336(5)	0.4497(5)	0.052(4)
C(15)	0.6564(6)	0.1012(5)	0.4842(5)	0.053(4)
N(21)	0.7254(4)	0.2401(4)	0.3370(4)	0.038(3)
N(22)	0.6506(4)	0.2183(3)	0.2463(3)	0.040(3)
C(23)	0.7058(6)	0.2180(6)	0.2020(5)	0.059(4)
C(24)	0.8138(7)	0.2379(6)	0.2588(6)	0.069(5)
C(25)	0.8235(6)	0.2509(6)	0.3449(6)	0.060(4)
N(31)	0.6171(4)	0.3238(3)	0.3969(3)	0.035(3)
N(32)	0.6251(5)	0.4046(4)	0.3626(4)	0.057(3)
C(33)	0.5595(7)	0.4597(5)	0.3749(5)	0.059(4)
C(34)	0.5127(7)	0.4159(6)	0.4194(6)	0.062(5)
C(35)	0.5476(7)	0.3306(5)	0.4301(5)	0.054(4)
N(41)	0.7990(5)	0.2572(4)	0.5081(4)	0.045(3)
N(42)	0.8730(5)	0.1898(5)	0.5453(3)	0.061(3)
C(43)	0.9615(6)	0.2275(6)	0.6160(5)	0.061(4)
C(44)	0.9462(6)	0.3184(6)	0.6231(5)	0.060(4)
C(45)	0.8411(6)	0.3353(5)	0.5529(5)	0.054(4)

[a] Site occupancy factors: $C = 0.945(2)$, $I = 1 - 0.945(2)$.

Table 3
Non-hydrogen atom coordinates and equivalent isotropic displacement parameters for PdPh{$(pz)_3BH$}(PPh_3) (**3**)

Atom	x	y	z	U_{eq} (Å^2)
Pd	0.16089(5)	0.18208(7)	0.17497(8)	0.0381(2)
P(1)	0.2920(2)	0.0876(2)	0.1175(3)	0.0415(9)
C(111)	0.3421(6)	−0.0308(8)	0.2208(9)	0.046(4)
C(112)	0.2958(7)	−0.1400(9)	0.235(1)	0.062(4)
C(113)	0.3349(8)	−0.2317(9)	0.311(1)	0.069(5)
C(114)	0.4227(9)	−0.213(1)	0.373(1)	0.073(5)
C(115)	0.4697(8)	−0.108(1)	0.359(1)	0.076(5)
C(116)	0.4310(8)	−0.0160(9)	0.284(1)	0.067(5)
C(121)	0.2827(6)	0.0188(8)	−0.0571(9)	0.042(3)
C(122)	0.3416(7)	−0.0707(9)	−0.104(1)	0.056(4)
C(123)	0.3349(7)	−0.114(1)	−0.239(1)	0.070(5)
C(124)	0.2707(8)	−0.065(1)	−0.329(1)	0.071(5)
C(125)	0.2109(8)	0.023(1)	−0.284(1)	0.067(5)
C(126)	0.2168(6)	0.0657(8)	−0.1471(9)	0.047(4)
C(131)	0.3848(6)	0.2025(8)	0.115(1)	0.043(4)
C(132)	0.4406(7)	0.2174(9)	0.007(1)	0.057(4)
C(133)	0.5065(8)	0.310(1)	0.010(1)	0.071(5)
C(134)	0.5172(8)	0.389(1)	0.124(2)	0.078(6)
C(135)	0.4610(8)	0.377(1)	0.232(1)	0.081(5)
C(136)	0.3956(7)	0.2841(9)	0.231(1)	0.055(4)
C(1)	0.1101(6)	0.0215(8)	0.2190(9)	0.043(4)
C(2)	0.1010(8)	−0.0113(9)	0.351(1)	0.059(4)
C(3)	0.0547(8)	−0.119(1)	0.381(1)	0.074(5)
C(4)	0.0187(8)	−0.1975(9)	0.277(1)	0.065(5)
C(5)	0.0297(6)	−0.1693(9)	0.146(1)	0.056(4)
C(6)	0.0739(6)	−0.0616(8)	0.1154(9)	0.045(4)
B	0.1288(9)	0.463(1)	0.310(1)	0.059(5)
N(11)	0.1717(5)	0.4610(7)	0.1699(8)	0.055(3)
N(12)	0.1984(5)	0.3557(7)	0.1057(8)	0.050(3)
C(13)	0.2289(7)	0.3863(9)	−0.013(1)	0.056(4)
C(14)	0.2235(8)	0.511(1)	−0.028(1)	0.070(5)
C(15)	0.1864(8)	0.5531(9)	0.091(1)	0.072(5)
N(21)	0.0405(6)	0.3802(7)	0.2996(8)	0.055(3)
N(22)	0.0401(5)	0.2634(7)	0.2465(7)	0.046(3)
C(23)	−0.462(7)	0.2219(9)	0.2518(9)	0.050(4)
C(24)	−0.1027(7)	0.310(1)	0.309(1)	0.064(5)
C(25)	−0.0459(8)	0.408(1)	0.336(1)	0.061(4)
N(31)	0.1984(6)	0.4192(7)	0.4252(8)	0.055(3)
N(32)	0.2732(7)	0.4920(9)	0.459(1)	0.088(5)
C(33)	0.3173(9)	0.434(1)	0.559(1)	0.090(6)
C(34)	0.273(1)	0.327(1)	0.558(1)	0.083(6)
C(35)	0.1979(8)	0.323(1)	0.498(1)	0.070(5)

For each complex a unique data set was measured at 295 K using an Enraf-Nonius CAD-4 diffractometer operating in conventional $2\theta-\theta$ scan mode with monochromatic Mo K_α radiation ($\lambda = 0.71073$ Å), yielding N independent reflections, N_o with $I > 3\sigma(I)$ considered observed and used in the full matrix least-squares refinement after analytical absorption correction, and solution of the structures by vector methods.

Residuals R and R_w are quoted on $|F|$ at convergence; statistical weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\ \sigma^4(I_{diff})$ were employed. Neutral atom complex scattering factors were used [10]; computation used the XTAL 3.0 program system implemented by Hall [11]. Crystal data, coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms, and geometries of the complexes are given in Tables 1–5, and views of the complexes are shown in Figs. 1 and 2.

Table 4
Non-hydrogen atom coordinates and equivalent isotropic displacement parameters for PdPh{$(pz)_4B$}(PPh_3) (**4**)

Atom	x	y	z	U_{eq} (Å^2)
Pd	0.71602(1)	0.95938(3)	0.83707(1)	0.03463(7)
P(1)	0.82955(4)	0.99346(9)	0.89612(4)	0.0357(2)
C(111)	0.8621(2)	1.1816(3)	0.9212(1)	0.038(1)
C(112)	0.8398(2)	1.2458(4)	0.9748(2)	0.052(1)
C(113)	0.8617(2)	1.3891(4)	0.9936(2)	0.063(1)
C(114)	0.9055(2)	1.4687(4)	0.9594(2)	0.070(2)
C(115)	0.9276(2)	1.4072(4)	0.9065(2)	0.073(2)
C(116)	0.9055(2)	1.2639(4)	0.8868(2)	0.055(1)
C(121)	0.8369(2)	0.8928(3)	0.9725(1)	0.037(1)
C(122)	0.8947(2)	0.9174(4)	1.0240(2)	0.048(1)
C(123)	0.8966(2)	0.8431(4)	1.0821(2)	0.058(1)
C(124)	0.8409(2)	0.7429(4)	1.0890(2)	0.057(1)
C(125)	0.7843(2)	0.7176(4)	1.0384(2)	0.056(1)
C(126)	0.7819(2)	0.7925(4)	0.9805(2)	0.046(1)
C(131)	0.9032(2)	0.9223(3)	0.8555(1)	0.039(1)
C(132)	0.9632(2)	0.8410(4)	0.8868(2)	0.048(1)
C(133)	1.0176(2)	0.7917(4)	0.8531(2)	0.065(2)
C(134)	1.0121(2)	0.8234(5)	0.7884(2)	0.074(2)
C(135)	0.9524(2)	0.9028(5)	0.7567(2)	0.070(2)
C(136)	0.8977(2)	0.9518(4)	0.7897(2)	0.055(1)
C(1)	0.6863(2)	1.1441(4)	0.8792(1)	0.039(1)
C(2)	0.6891(2)	1.2811(4)	0.8488(2)	0.047(1)
C(3)	0.6657(2)	1.4116(4)	0.8743(2)	0.061(1)
C(4)	0.6381(2)	1.4055(5)	0.9310(2)	0.074(2)
C(5)	0.6346(2)	1.2722(6)	0.9619(2)	0.071(2)
C(6)	0.6583(2)	1.1406(4)	0.9368(2)	0.055(1)
B	0.6512(2)	0.8441(4)	0.6894(2)	0.037(1)
N(11)	0.7140(1)	0.7430(3)	0.7242(1)	0.0369(8)
N(12)	0.7426(1)	0.7649(3)	0.7884(1)	0.0414(9)
C(13)	0.7910(2)	0.6545(4)	0.8047(2)	0.050(1)
C(14)	0.7951(2)	0.5629(4)	0.7532(2)	0.056(1)
C(15)	0.7457(2)	0.6216(4)	0.7031(2)	0.050(1)
N(21)	0.5906(1)	0.8622(3)	0.7318(1)	0.0376(8)
N(22)	0.6068(1)	0.9271(3)	0.7914(1)	0.0395(8)
C(23)	0.5426(2)	0.9516(4)	0.8111(2)	0.047(1)
C(24)	0.4841(2)	0.9042(4)	0.7638(2)	0.055(1)
C(25)	0.5159(2)	0.8491(4)	0.7149(2)	0.046(1)
N(31)	0.6795(1)	1.0005(3)	0.6781(1)	0.0381(8)
N(32)	0.7461(2)	1.0235(3)	0.6597(1)	0.053(1)
C(33)	0.7467(2)	1.1689(4)	0.6460(2)	0.064(2)
C(34)	0.6824(2)	1.2401(4)	0.6543(2)	0.061(1)
C(35)	0.6413(2)	1.1291(4)	0.6746(2)	0.051(1)
N(41)	0.6169(1)	0.7734(3)	0.6249(1)	0.0418(9)
N(42)	0.5969(2)	0.6262(3)	0.6203(1)	0.055(1)
C(43)	0.5677(2)	0.6058(5)	0.5589(2)	0.063(1)
C(44)	0.5674(2)	0.7349(5)	0.5232(2)	0.068(2)
C(45)	0.5991(2)	0.8398(4)	0.5667(2)	0.054(1)

Table 5
Non-hydrogen atom coordinates and equivalent isotropic displacement parameters for Pd(η^3-C_3H_5){$(pz)_3BH$} (**5**)

Atom	x	y	z	U_{eq} (Å^2)
Pd	0.57601(4)	0.44118(4)	−0.12550(9)	0.0391(2)
B	0.6528(7)	0.3871(6)	0.213(1)	0.038(4)
N(11)	0.6603(5)	0.4692(4)	0.1737(9)	0.038(3)
N(12)	0.6470(5)	0.4940(4)	0.030(1)	0.040(3)
C(13)	0.6747(6)	0.5614(6)	0.024(1)	0.044(3)
C(14)	0.7046(6)	0.5799(6)	0.166(1)	0.052(4)
C(15)	0.6955(6)	0.5204(6)	0.254(1)	0.051(4)
N(21)	0.5730(5)	0.3585(4)	0.1836(9)	0.041(3)
N(22)	0.5375(4)	0.3694(4)	0.045(1)	0.040(3)
C(23)	0.4759(6)	0.3337(6)	0.052(1)	0.047(4)
C(24)	0.4678(7)	0.2976(6)	0.192(1)	0.052(4)
C(25)	0.5304(7)	0.3144(6)	0.269(1)	0.054(4)
N(31)	0.7078(4)	0.3425(4)	0.117(1)	0.039(3)
N(32)	0.7813(5)	0.3602(5)	0.121(1)	0.057(3)
C(33)	0.8151(6)	0.3136(7)	0.029(1)	0.055(4)
C(34)	0.7643(8)	0.2658(6)	−0.039(1)	0.058(5)
C(35)	0.6983(7)	0.2862(6)	0.019(2)	0.062(5)
C(1)	0.5913(9)	0.5074(8)	−0.321(1)	0.078(6)
C(2)	0.566(1)	0.4462(7)	−0.363(1)	0.113(7)
C(3)	0.5082(7)	0.4085(7)	−0.309(1)	0.060(4)

Tables of thermal parameters and calculated hydrogen atom positions, and details of the ligand geometries, have been deposited with the Cambridge Crystallographic Data Centre.

3. Results and discussion

The complexes $[PdMe(SMe_2)(\mu\text{-}X)]_2$ (X = Cl, Br, I) [8] and PdIPh(tmeda) [9] have been reported to be ideal substrates for the synthesis of methyl- and phenyl-palladium(II) complexes [9,12–18], and the required poly(pyrazol-1-yl)borate complexes were readily obtained by use of these substrates, as shown in Eqs. (1) and (2).

$$\begin{aligned} &1/2[PdMe(SMe_2)(\mu\text{-}I)]_2 + K[(pz)_3BR] \\ &\quad + PPh_3 + TlPF_6 \\ &\quad \longrightarrow PdMe\{(pz)_3BR\}(PPh_3) \\ &\qquad + TlI + KPF_6 + SMe_2 \qquad R = H\ (\mathbf{1}),\ pz\ (\mathbf{2}) \end{aligned} \tag{1}$$

$$\begin{aligned} &PdIPh(tmeda) + K[(pz)_3BR] + PPh_3 \\ &\quad \longrightarrow PdPh\{(pz)_3BR\}(PPh_3) + KI + tmeda \\ &R = H\ (\mathbf{3}),\ pz\ (\mathbf{4}) \end{aligned} \tag{2}$$

All the complexes exhibit a single environment for the pyrazole rings in ^1H NMR spectra, and for the tetrakis(pyrazol-1-yl)borate complexes the resonances for these protons are broad, consistent with the expected stereochemical nonrigidity as observed for related palladium(II) complexes of tripodal nitrogen donor ligands [1,2,15].

Table 6
Coordination geometry for the palladium atom in PdMe{(pz)$_4$B}(PPh$_3$) (**2**), PdPh{(pz)$_3$BH}(PPh$_3$) (**3**), and PdPh{(pz)$_4$B}(PPh$_3$) (**4**)

	(**2**) [a]	(**3**)	(**4**)
Distances (Å) [b]			
Pd–C(1)	2.02(2)	1.973(9)	1.990(3)
Pd–P(1)	2.248(3)	2.249(4)	2.2452(9)
Pd–N(12), N(22)	2.153(6), 2.078(6)	2.126(8), 2.100(8)	2.113(3), 2.079(2)
Angles (°)			
C(1)–Pd–P(1)	85.3(6)	87.9(3)	86.64(8)
C(1)–Pd–N(12), N(22)	171.7(5), 87.1(6)	171.4(3), 89.1(3)	176.93(9), 90.2(1)
P(1)–Pd–N(12), N(22)	101.9(2), 172.4(2)	96.4(2), 174.7(2)	96.23(7), 174.07(7)
N(12)–Pd–N(22)	85.7(2)	87.1(3)	87.0(1)
Pd–P(1)–C(111), C(121)	110.5(2), 117.2(3)	121.5(3), 112.1(3)	120.42(9), 109.7(1)
Pd–P(1)–C(131)	115.5(2)	108.3(3)	112.5(1)
Pd–N(12)–N(11), C(13)	119.5(4), 134.3(4)	122.0(6), 130.4(7)	120.7(2), 133.1(2)
Pd–N(22)–N(21), C(23)	120.8(5), 134.0(4)	121.8(6), 132.0(6)	121.3(2), 131.8(2)
Pd–C(1)–C(2), C(6)		122.5(7), 121.3(7)	119.7(2), 122.4(3)
Distances (Å) from the mean coordination planes 'PdCN$_2$P'			
Pd	−0.002(1)	−0.001(1)	0.025(1)
C	0.13(2)	−0.16(1)	−0.059(4)
P	0.002(3)	0.013(3)	0.017(1)
N(12), N(22)	0.013(8), 0.022(7)	−0.11(1), 0.138(8)	−0.029(3), 0.118(3)
Distances (Å) of palladium from the 'C$_3$N$_2$' mean planes of coordinated pz groups			
Ring 1	0.05(1)	0.41(2)	0.224(5)
Ring 2	0.12(1)	0.00(2)	0.085(5)
Dihedral angles (°) between coordination planes and pz and phenyl planes			
Ring 1	41.7(2)	43.1(3)	37.1(1)
Ring 2	42.0(3)	32.7(3)	33.4(1)
Phenyl		76.6(3)	89.2(1)

[a] Refined as PdI$_{0.05}$Me$_{0.95}${(pz)$_4$B}(PPh$_3$). Pd–I = 2.49(2) Å.
[b] Shortest intramolecular contacts from Pd to uncoordinated pz ring: Pd...N(31) = 3.295(6) (**2**), 3.491(8) (**3**), 3.297(3) Å (**4**). Complex (**2**) has C(34)...H(116) ~ 2.67 and N(32)...H(136) ~ 2.73 Å.

The crystal of complex (**2**) examined by X-ray diffraction is apparently an impure sample of PdMe{(pz)$_4$B}(PPh$_3$), containing a small amount of iodide in place of a methyl group (Table 1). Thus structural parameters for the major component of the crystal, PdMe{(pz)$_4$B}(PPh$_3$), are less accurate than those for

Table 7
Coordination geometry for the palladium atom in Pd(η^3-C$_3$H$_5$){(pz)$_3$BH} (**5**) [a]

Distances (Å)			
Pd–C(1)	2.10(1)	Pd–N(12)	2.091(8)
Pd–C(2)	2.06(1)	Pd–N(22)	2.095(8)
Pd–C(3)	2.09(1)		
Angles (°)			
C(1)–Pd–C(2)	35.4(5)	C(1)–Pd–N(12), N(22)	99.8(4), 166.9(5)
C(1)–Pd–C(3)	68.3(5)	C(2)–Pd–N(12), N(22)	132.3(5), 134.4(5)
C(2)–Pd–C(3)	37.4(6)	C(3)–Pd–N(12), N(22)	167.7(4), 99.4(4)
C(1)–C(2)–C(3)	130(1)	N(12)–Pd–N(22)	92.2(3)
Pd–C(1)–C(2)	70.8(8)	Pd–N(12)–N(11), C(13)	123.1(6), 129.0(7)
Pd–C(2)–C(1), C(3)	73.8(8), 72.3(7)	Pd–N(22)–N(21), C(23)	123.6(6), 129.5(7)
Pd–C(3)–C(2)	70.4(8)		
Distances (Å) from the plane 'PdN(12)N(22)'			
C(1)	−0.19(2)	C(3)	0.14(2)
C(2)	0.28(2)		
Distances (Å) of palladium from the 'C$_3$N$_2$' mean planes of coordinated pz groups			
ring 1	0.32(2)	ring 2	0.17(2)
Dihedral angles (°) between angles			
'C(1)C(2)C(3)'/'PdN(12)N(22)'	125.5(2.1)	'ring 1'/'ring 2'	144.0(5)
'ring 1'/'PdN(12)N(22)	18.8(4)	'ring 1'/'ring 3'	96.4(5)
'ring 2'/'PdN(12)N(22)	20.3(4)	'ring 2'/'ring 3'	74.1(5)
'ring 3'/'PdN(12)N(22)	109.5(4)		

[a] Shortest intramolecular contact from Pd to uncoordinated pz ring: Pd...N(31) = 3.641(8) Å.

the PhPd(II) complexes (Table 5), and are even less reliable for the minor component, PdI{(pz)$_4$B}(PPh$_3$), which has Pd–I 2.49(2) Å compared with 2.5703(8) Å and 2.575(1) Å for the related complexes PdIPh(tmeda) and PdIPh(bpy) (bpy = 2,2′-bipyridyl), respectively [9].

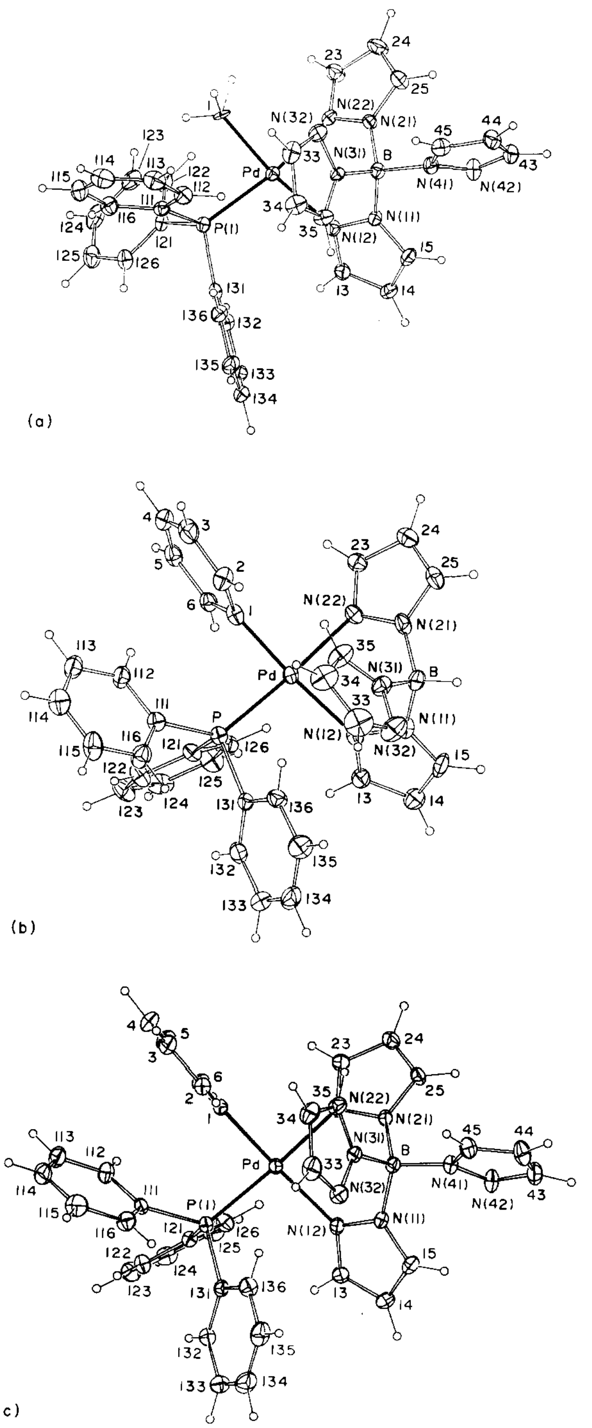

Fig. 1. The molecular structures of (a) PdMe{(pz)$_4$B}(PPh$_3$) (2), (b) PdPh{(pz)$_3$BH}(PPh$_3$) (3), and (c) PdPh{(pz)$_4$B}(PPh$_3$) (4) projected normal to the coordination plane. Hydrogen atoms are shown with an arbitrary radius of 0.1 Å, and 20% thermal ellipsoids are shown for the non-hydrogen atoms.

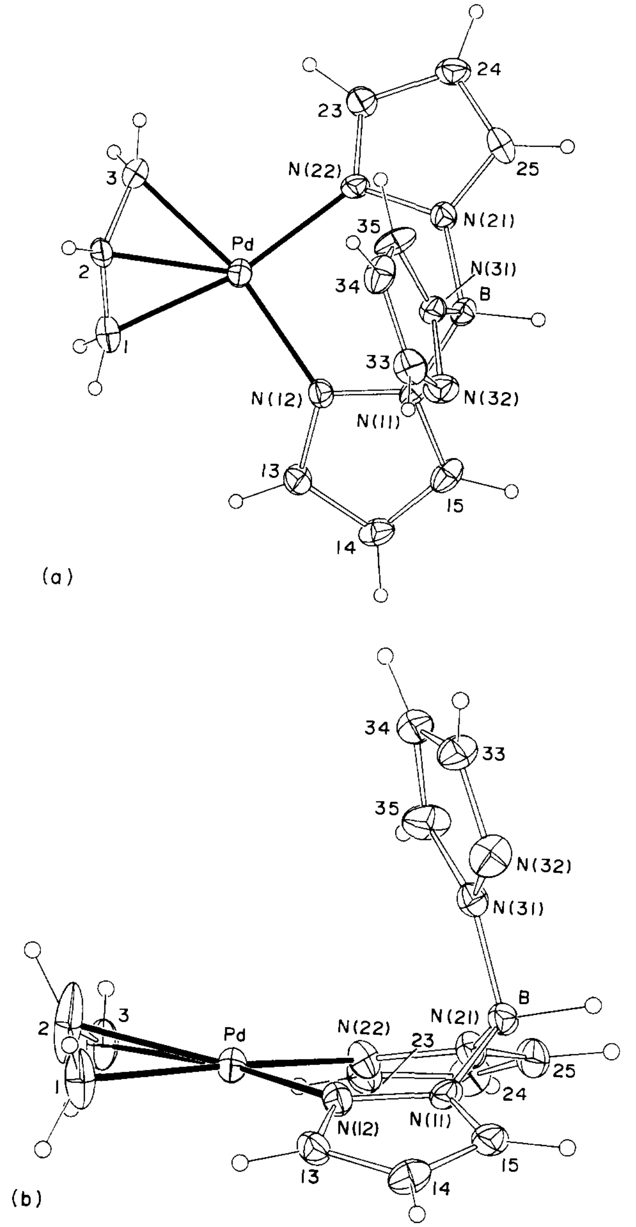

Fig. 2. Two views of the molecular structure of Pd(η^3-C$_3$H$_5$){(pz)$_3$BH} (5), where (a) is a projection normal to the 'PdN$_2$' plane.

Aspects of the coordination geometry for the complexes are presented in Tables 6 and 7.

The poly(pyrazol-1-yl)borate ligands form chelate angles of ca. 86–87° for (2)–(4) and 92.2(3)° for (5), and adopt a boat conformation for the six-membered PdN$_4$B rings in which the uncoordinated ring in (3) and (5) lie above the coordination plane ('axial') rather than in the alternative 'equatorial' position (Fig. 1(b) and 1(d)). A similar axial orientation for uncoordinated planar groups is found in other structural studies of related square planar d^8 complexes of tripod ligands, e.g. $Pd\{(pz)_2BH\text{-}N,N'\}_2$, $[Pd(L_3\text{-}N,N')_2]^{2+}$ [L_3 = $(pz)_3CH$, tris(pyridin-2-yl)methane] [19], $[PdCl_2\{(py)_2(pyH)CH\text{-}N,N'\}]^+$ [$(py)_2(pyH)CH$ = monoprotonated tris(pyridin-2-yl)methane] [20], $AuMe_2\{(pz)_3BH\text{-}N,N'\}$ [19], and $[AuMe_2(L_3\text{-}N,N')]^+$ (L_3 = tris(pyridin-2-yl)methanol [21] and tris (*N*-methylimidazol-2-yl)methanol [22]).

Palladium–carbon bond lengths in complexes **(2)**–**(4)** are within 1σ of those reported for the related methyl- and phenylpalladium(II) bidentate nitrogen donor complexes $PdIPh(L_2)$ (L_2 = tmeda, bpy) [9], $[PdMe(bpy)(\gamma\text{-picoline})]BF_4$ [16] and PdClMe(2,9-dimethyl-1,10-phenanthroline) [23]. The largest deviations from the mean coordination planes '$PdCN_2P$' are exhibited by C in **(2)** [0.13(2) Å] and **(3)** [−0.16(1) Å] and N(22) in **(4)** [0.118(3) Å]. The phenyl rings form dihedral angles of 76.6(3)° **(3)** and 89.2(1)° **(4)** with the coordination planes, and the coordinated pyrazole rings form dihedral angles of 32.7(3)–42.0(3)° with the coordination planes. The uncoordinated pyrazole rings above the coordination plane form dihedral angles of 56.2(3)° **(2)**, 60.1(4)° **(3)** and 60.1(1)° **(4)** with the coordination planes.

In the η^3-allylpalladium(II) complex **(5)** the 'PdN_2' plane forms dihedral angles of 18.8(4) and 20.3(4)° with the coordinated pyrazole planes, and 109.5(4)° with the uncoordinated pyrazole plane. The η^3-allylpalladium (II) geometry is similar to that found in related complexes of bidentate nitrogen donor ligands [3,24–29]. In particular, the allyl plane is not normal the 'PdN_2' plane, forming a dihedral angle of 125.5(2.1)° with the central C–H tilted away from palladium, and the central carbon forms a shorter Pd–C bond [2.06(1) Å] than the outer carbon atoms (2.09(1), 2.10(1) Å). The central carbon atoms lies 0.28(2) Å to one side of the 'PdN_2' plane, and the outer carbon atoms lie 0.19(2) and 0.14(2) Å to the other side of the plane. Librational amplitudes for the allyl group are very large, possibly a result of unresolved disorder, and thus the calculated geometries should be treated with caution.

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References

[1] S. Trofimenko, *J. Am. Chem. Soc.*, *91* (1969) 588.
[2] P.K. Byers, A.J. Canty and R.T. Honeyman, *Adv. Organomet. Chem.*, *34* (1992) 1.
[3] J.-M. Valk, F. Maassarani, P. van der Sluis, A.L. Spek, J. Boersma and G. van Koten, *Organometallics*, *13* (1994) 2320.
[4] A.J. Canty, R.T. Honeyman, R. Colton, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, *471* (1994) C8.
[5] C.P. Brock, M.K. Das, R.P. Minton and K. Niedenzu, *J. Am. Chem. Soc.*, *110* (1988) 817.
[6] A.J. Canty, *Acc. Chem. Res.*, *25* (1992) 83.
[7] A.J. Canty and P.R. Traill, *J. Organomet. Chem.*, *435* (1992) C8.
[8] P.K. Byers, A.J. Canty, L.M. Engelhardt and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1986) 1731.
[9] B.A. Markies, A.J. Canty, W. de Graaf, J. Boersma, M.D. Janssen, M.P. Hogerheide, W.J.J. Smeets, A.L. Spek and G. van Koten, *J. Organomet. Chem.*, (1994) in press.
[10] J.A. Ibers and W.C. Hamilton (eds.), *International Tables for X-ray Crystallography*, Vol. 4, Kynoch, Birmingham, 1974.
[11] S.R. Hall and J.M. Stewart, *The XTAL Users Manual, Version 3.0*, Universities of Western Australia and Maryland, 1990.
[12] P.K. Byers, A.J. Canty, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, *336* (1987) C55.
[13] P.K. Byers and A.J. Canty, *Organometallics*, *9* (1990) 210.
[14] P.K. Byers, A.J. Canty, B.W. Skelton, P.R. Traill, A.A. Watson and A.H. White, *Organometallics*, *9* (1990) 3080.
[15] P.K. Byers, A.J. Canty and R.T. Honeyman, *J. Organomet. Chem.*, *385* (1990) 417.
[16] P.K. Byers, A.J. Canty, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, *393* (1990) 299.
[17] V.G. Albano, C. Castellari, M.E. Cucciolito, A. Panunzi and A. Vitagliano, *Organometallics*, *9* (1990) 1269.
[18] W. de Graaf, J. van Wegen, J. Boersma, A.L. Spek and G. van Koten, *Recl. Trav. Chim. Pays-Bas*, *108* (1989) 275.
[19] A.J. Canty, N.J. Minchin, L.M. Engelhardt, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1986) 645.
[20] A.J. Canty, N.J. Minchin, B.W. Skelton and A.H. White, *Aust. J. Chem.*, *45* (1992) 423.
[21] A.J. Canty, N.J. Minchin, J.M. Patrick and A.H. White, *Aust. J. Chem.*, *36* (1983) 1251.
[22] A.J. Canty, N.J. Minchin, P.C. Healy and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1982) 1795.
[23] V. De Felice, V.G. Albano, C. Castellari, M.E. Cucciolito and A. De Renzi, *J. Organomet. Chem.*, *403* (1991) 269.
[24] S.C. De Sanctis, N.V. Pavel and L. Toniolo, *J. Organomet. Chem.*, *108* (1976) 409.
[25] L.S. Hegedus, B. Akermark, D.J. Olsen, O.P. Anderson and K. Zetterberg, *J. Am. Chem. Soc.*, *104* (1982) 697.
[26] B. Crociani, R. Bertani, T. Boschi and G. Bandoli, *J. Chem. Soc., Dalton Trans.*, (1982) 1715.
[27] A. Albinati, C. Ammann, P.S. Pregosin and H. Ruegger, *Organometallics*, *9* (1990) 1826.
[28] A. Togni, G. Rihs, P.S. Pregosin and C. Ammann, *Helv. Chim. Acta*, *73* (1990) 723.
[29] A. Albinati, R.W. Kunz, C.J. Ammann and P.S. Pregosin, *Organometallics*, *10* (1991) 1800.