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Synthesis and reactivity of poly(pyrazol-1-yl) borate derivatives of cyclopalladation systems, including structural studies of Pd{2-$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C*,*P*}{$(pz)_3$BH-*N*,*N*′} and Pd($C_6H_4C_5H_4N$-C^2,*N*′){$(pz)_3$BH-*N*,*N*′}

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Abstract

The cyclopalladated complexes Pd{2-$CH_2C_6H_4P$(*o*-tol)$_2$}{$(pz)_nBH_{4-n}$} and Pd($C_6H_4C_5H_4N$-C^2,*N*′){$(pz)_nBH_{4-n}$} [$n = 2$, 3; pz = pyrazol-1-yl] have been synthesised from the corresponding halide bridged cyclometallated dimers; the crystal structures of the complexes for which $n = 3$ have been determined. The complexes Pd{2-$CH_2C_6H_4P$(*o*-tol)$_2$}{$(pz)_nBH_{4-n}$} ($n = 2$, 3) and [Pd{2-$CH_2C_6H_4P$(*o*-tol)$_2$}(μ-O_2CMe)]$_2$ are unreactive towards oxidation by alkyl halides, iodobenzene and 4-bromoanisole. © 1998 Elsevier Science S.A.

Keywords: Palladium; Cyclopalladation; Tris(*o*-tolyl)phosphine; Poly(pyrazol-1-yl)borate; Crystal structure

1. Introduction

Palladium(II) complexes containing cyclopalladated tris(*o*-tolyl)phosphine, e.g., [Pd{2-$CH_2C_6H_4P$(*o*-tol)$_2$}(μ-O_2CMe)]$_2$ have shown considerable promise as catalysts for organic synthesis [1–7]. There is much current interest in these catalysts as they involve significant advances in the development of important processes such as Heck and Suzuki catalysis. It was initially proposed that for some of these systems Pd(IV) species may occur as undetected intermediates [1,2,5], although recent work has indicated that catalysis via Pd(0) and Pd(II) species cannot be discounted [6,8]. Organopalladium(IV) complexes containing 'soft' phosphine donor ligands have not been isolated or detected spectroscopically, and thus there is a lack of ideal 'model complexes' for potential intermediates in these catalyses. However, a complex containing soft thioether donor atoms has been isolated, [$PdMe_3$(1,4,7-trithiacyclononane)] [9,10], and a silylpalladium(IV) complex containing a bidentate phosphine synthesized and characterized by X-ray diffraction, Pd{1,2-$(SiH_2)_2C_6H_4$-*Si*,*Si*′}{$(PMe_2CH_2)_2$-*P*,*P*′)} [11].

Some of the most stable organopalladium(IV) complexes known contain poly(pyrazol-1-yl)borate ligands [12,13], as they give enhanced nucleophilic character for Pd(II) substrates to facilitate oxidative addition reactions, and tripodal coordination stabilizes the octahedral Pd(IV) products, e.g., on reaction of iodoethane with [$PdMe_2${$(pz)_3$BH}]$^-$ to form $PdMe_2Et${$(pz)_3$BH} [12]. Thus, in a study exploring the potential for Pd(IV) chemistry containing cyclopalladated tris(*o*-tolyl)phosphine, we have examined the reactivity of Pd{2-$CH_2C_6H_4P$(*o*-tol)$_2$-*C*,*P*}{$(pz)_3$BH} (**1**) and Pd{2-$CH_2C_6H_4P$(*o*-tol)$_2$-*C*,*P*}{$(pz)_2BH_2$} (**3**) toward oxidizing agents. As part of this study, we have included palladated 2-phenylpyridine as a classic nitrogen donor system for comparison [14–22], Pd($C_6H_4C_5H_4N$-C^2,*N*′){$(pz)_nBH_{4-n}$} [$n = 3$, (**2**); $n = 2$, (**4**)], and structural studies of the tris(pyrazol-1-yl)borate complexes of the [C–P]$^-$ and [C–N]$^-$ ligands have been determined.

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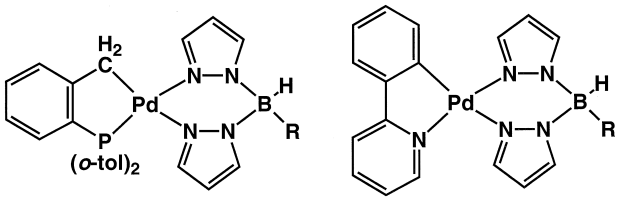
2. Experimental

Unless otherwise stated, reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques in solvents purified according to standard procedures. The reagents K[$(pz)_3BH$] and K[$(pz)_2BH_2$] [23], phenyliodonium dichloride [24], the cyclopalladated 2-phenylpyridine complex [Pd($C_6H_4C_5H_4N$-C^2,N')(μ-Cl)]$_2$ [22], and the cyclopalladated P(*o*-tol)$_3$ complexes [Pd{2-$CH_2C_6H_4P$(*o*-tol)$_2$}(μ-O_2CMe)]$_2$ and [Pd{2-$CH_2C_6H_4P$(*o*-tol)$_2$}(μ-Br)]$_2$ [1] were prepared as described. Microanalyses were by the Central Science Laboratory, University of Tasmania, and NMR spectra were recorded with a Bruker AM 300 spectrometer, with chemical shifts given in ppm relative to $SiMe_4$ (^{1}H, ^{13}C) or external H_3PO_4 (^{31}P).



2.1. Synthesis of complexes

2.1.1. Pd{2-$CH_2C_6H_4P$(*o*-tol)$_2$}{$(pz)_3BH$} (1)

A solution of [Pd{$CH_2(C_6H_4)$P(*o*-tol)$_2$}(μ-Br)]$_2$ (0.15 g, 0.15 mmol) and K[$(pz)_3BH$] (0.12 g, 0.48 mmol) in acetone (30 ml) was stirred at room temperature for 24 h, after which a fine white precipitate was removed by filtration. The solvent was removed in vacuo and the residue was extracted with diethyl ether. Filtration and removal of solvent in vacuo gave the product as a white crystalline solid (0.19 g, 100%). Anal. Found: C, 58.0; H, 4.9; N, 13.6. $C_{30}H_{30}BN_6PPd$. Calc.: C, 57.9; H, 4.9; N, 13.5 %. ^{1}H NMR (CD_2Cl_2, 233 K) δ 7.52 (d, ^3J = 2.1 Hz, 3, $H3_{pz}$), 7.40 (m, br, 6, H_{tolyl}) and 7.18 (br, 3, $H5_{pz}$) and 7.11 (m, br, 3, H_{tolyl}) overlapping, 6.82 ('t', ^3J = 9.7 Hz, 3, H_{tolyl}), 6.00 (br, 3, $H4_{pz}$), 3.46 (s, 2, PdCH_2), 2.57 (s, 3, CH_3), 1.63 (s, 3, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 233 K) δ 158.0 (d, $^1J_{PC}$ = 31.3 Hz, *C*–P), 148.9, 143.9, 143.0, 142.8 (C_{tolyl}), 141.4 (br, Cpz), 136.7, 135.6, 135.0, 133.8 (C_{tolyl}), 133.1 (br, Cpz), 132.9, 132.6, 131.9, 129.3 (d, J_{PC} = 23.1 Hz), 127.4, 127.0 (d, J_{PC} = 8.0 Hz) (C_{tolyl}), 105.0 (br, Cpz), 31.68 (Pd–*C*), 23.6 (d, J_{PC} = 11.3 Hz, *C*H_3), 23.2 (d, J_{PC} = 8.3 Hz, *C*H_3). ^{31}P{^{1}H} NMR (acetone-d_6) δ 40.0.

2.1.2. Pd{$C_6H_4C_5H_4N$-C^2,N'}{$(pz)_3BH$} (2)

A solution of [Pd($C_6H_4C_5H_4N$-C^2,N')(μ-Cl)]$_2$ (0.18 g, 0.32 mmol) and K[$(pz)_3BH$] (0.20 g, 0.79 mmol) in acetone (30 ml) was stirred at room temperature for 24 h, after which a pale yellow precipitate was removed by filtration. The solvent was removed in vacuo and the residue extracted with diethyl ether. Filtration and removal of solvent in vacuo gave the product as a pale yellow solid (0.14 g, 50%). Anal. Found: C, 51.1; H, 4.5; N, 20.9. $C_{20}H_{18}BN_7Pd$. Calc.: C, 50.7; H, 3.8; N, 20.7 %. ^{1}H NMR ($CDCl_3$) δ 8.38 (d, ^3J = 4.9 Hz, 1, $H6_{py}$), 7.79 (m, 5, H_{Phpy}) and 7.68 (br, 3, $H3_{pz}$) overlapping, 7.52 (m, 1, H_{Phpy}), 7.14 (m, 4, H_{Phpy} and $H5_{pz}$ overlapping), 6.29 ('t', 3, $H4_{pz}$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 166.7, 155.5, 150.2 ($C6_{py}$), 146.2, 142.0 (br, C3), 139.5, 136.7 (br, C5), 135.3, 129.9, 125.5, 123.9, 122.6, 119.4, 105.8 (br, C4).

2.1.3. Pd{2-$CH_2C_6H_4P$(*o*-tol)$_2$}{$(pz)_2BH_2$} (3)

A solution of [Pd{$CH_2(C_6H_4)$P(*o*-tol)$_2$}(μ-Br)]$_2$ (0.24 g, 0.25 mmol) and K[$(pz)_2BH_2$] (0.10 g, 0.54 mmol) in acetone (30 ml) was stirred at room temperature for 24 h, after which a pale yellow precipitate was removed by filtration. The solvent was removed in vacuo and the residue extracted with diethyl ether. Filtration and removal of solvent in vacuo gave the product as a pale yellow solid (0.26 g, 96 %). Anal. Found: C, 58.4; H, 5.3; N, 9.8. $C_{27}H_{28}BN_4PPd$. Calc. C, 58.3; H, 5.1; N, 10.1 %. ^{1}H NMR (CD_2Cl_2, 233 K) δ 7.81 (d, ^3J = 2.0 Hz, 1, $H3_{pz}$), 7.61 (d, ^3J = 2.0 Hz, 1, $H3'_{pz}$), 7.49 (d, ^3J = 1.3 Hz, 1, $H5_{pz}$) and 7.41 (m, 5H, H_{tolyl}) and 7.33 (s, br, 1, $H5'_{pz}$, $H3_{pz}$) overlapping, 7.14 (m, 4, H_{tolyl}), 6.99 (m, 2H, H_{tolyl}), 6.48 (s, br, 1, H_{tolyl}), 6.29 (s, br, 1, $H4_{pz}$), 5.89 (s, br, 1, $H4'_{pz}$), 3.63 (d, $^2J_{HH}$ = 6.1 Hz, 1, PdCH_aH_b), 3.42 (d, $^2J_{HH}$ 6.9 Hz, 1, PdCH_aH_b), 2.72 (s, 3, CH_3), 2.08 (s, 3, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 233 K) δ 157.2 (d, J_{PC} = 33.7

Table 1
Crystal data and refinement parameters for Pd{2-$CH_2C_6H_4P$(*o*-tol)$_2$-*C,P*}{$(pz)_3BH$-*N,N'*} (**1**) and Pd($C_6H_4C_5H_4N$-*C*,^{2}*N'*){$(pz)_3BH$-*N,N'*}·0.5 Et_2O (**2**)

	(1)	(2)
Formula	$C_{30}H_{30}BN_6PPd$	$C_{20}H_{18}BN_7Pd\cdot0.5(C_4H_{10}O)$
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	9.299(2)	11.38(2)
b (Å)	22.513(8)	13.508(5)
c (Å)	13.945(6)	16.21(1)
β (°)	91.28(3)	115.07(8)
V (Å)	2919	2257
Z	4	4
Mol. wt.	622.8	510.69
$D_{calc.}$ (g cm^{-3})	1.41_7	1.50_3
Crystal size (mm)	0.48×0.18×0.18	0.26×0.11×0.17
μ (cm^{-1})	7.2	8.5
F (000)	1272	1036
$2\theta_{max}$ (°)	55	50
$A^*_{min,max}$	1.12, 1.14	1.11, 1.15
N, N_o	6677, 5123	3928, 2360
R, R_w	0.036, 0.035	0.056, 0.066

Table 2
Atom coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms of Pd{2-$CH_2C_6H_4P(o\text{-tol})_2$-*C,P*}{$(pz)_3BH$-*N,N′*} (**1**)

Atom	*x*	*y*	*z*	U_{eq}(Å^2)
Pd	0.77838(3)	0.70105(1)	0.36746(2)	0.03603(7)
N(1a)	0.7948(3)	0.8197(1)	0.4731(2)	0.0446(9)
N(2a)	0.7012(3)	0.7774(1)	0.4414(2)	0.0467(9)
C(3a)	0.5700(4)	0.7986(2)	0.4530(3)	0.063(1)
C(4a)	0.5764(5)	0.8551(2)	0.4918(3)	0.078(2)
C(5a)	0.7195(5)	0.8665(2)	0.5031(3)	0.066(1)
N(1b)	0.9981(3)	0.7998(1)	0.3630(2)	0.0410(8)
N(2b)	0.9306(3)	0.7579(1)	0.3082(2)	0.0397(8)
C(3b)	0.9895(4)	0.7602(1)	0.2220(2)	0.052(1)
C(4b)	1.0965(5)	0.8024(2)	0.2211(3)	0.066(1)
C(5b)	1.0995(4)	0.8267(1)	0.3110(3)	0.058(1)
N(1c)	1.0463(3)	0.8574(1)	0.5147(2)	0.0456(9)
N(2c)	1.0276(4)	0.9158(1)	0.4895(2)	0.062(1)
C(3c)	1.1258(4)	0.9451(2)	0.5404(3)	0.061(1)
C(4c)	1.2075(4)	0.9083(2)	0.5972(3)	0.071(2)
C(5c)	1.1551(4)	0.8527(2)	0.5789(3)	0.060(1)
B	0.9582(4)	0.8077(1)	0.4699(2)	0.042(1)
P	0.64215(9)	0.62834(3)	0.42547(5)	0.0364(2)
C(1d)	0.8524(4)	0.6336(2)	0.2826(2)	0.057(1)
C(2d)	0.7661(3)	0.5777(1)	0.2752(2)	0.041(1)
C(3d)	0.6538(3)	0.5695(1)	0.3372(2)	0.040(1)
C(4d)	0.5612(4)	0.5212(1)	0.3279(2)	0.053(1)
C(5d)	0.5823(5)	0.4801(1)	0.2558(3)	0.064(1)
C(6d)	0.6978(5)	0.4867(1)	0.1966(2)	0.063(1)
C(7d)	0.7903(4)	0.5345(1)	0.2060(2)	0.051(1)
C(1e)	0.4227(4)	0.6899(2)	0.2812(3)	0.065(1)
C(2e)	0.3647(4)	0.6650(1)	0.3725(2)	0.047(1)
C(3e)	0.4500(3)	0.6361(1)	0.4414(2)	0.0382(9)
C(4e)	0.3861(4)	0.6093(1)	0.5198(2)	0.044(1)
C(5e)	0.2391(4)	0.6120(2)	0.5317(2)	0.053(1)
C(6e)	0.1558(4)	0.6426(2)	0.4660(3)	0.063(1)
C(7e)	0.2178(4)	0.6683(2)	0.3874(3)	0.060(1)
C(1f)	0.6387(5)	0.6889(2)	0.6353(2)	0.067(1)
C(2f)	0.7116(4)	0.6296(1)	0.6251(2)	0.048(1)
C(3f)	0.7172(3)	0.5983(1)	0.5380(2)	0.041(1)
C(4f)	0.7906(4)	0.5445(1)	0.5349(3)	0.055(1)
C(5f)	0.8575(5)	0.5211(2)	0.6162(3)	0.073(2)
C(6f)	0.8511(5)	0.5516(2)	0.7016(3)	0.077(2)
C(7f)	0.7787(4)	0.6044(2)	0.7055(2)	0.064(1)

Hz, *C*–P), 142.3 (d, J_{PC} = 14.6 Hz, C_{tolyl}), 141.6 (d, J_{PC} = 12.2 Hz, C_{tolyl}), 138.7, 138.3, 135.7, 134.9, 134.0, 133.2, 132.7, 132.5, 131.8, 131.5, 131.3, 130.7, 128.3, 128.0, 127.7, 126.0, 125.6, 104.5 (C4,4′ pz), 29.7 (Pd*C*), 22.2 (br, CH_3). $^{31}P\{^1H\}$ NMR (acetone-d_6) δ 39.7.

2.1.4. *Pd{$C_6H_4C_5H_4N$-C^2,N'}{$(pz)_2BH_2$}* (**4**)

A solution of $[Pd(C_6H_4C_5H_4N\text{-}C^2,N')(\mu\text{-}Cl)]_2$ (0.21 g, 0.37 mmol) and $K[(pz)_2BH_2]$ (0.17 g, 0.91 mmol) in acetone (20 ml) was stirred at room temperature for 24 h, after which a precipitate was removed by filtration. The solvent was removed in vacuo and the residue extracted with diethyl ether. Filtration and removal of solvent in vacuo gave the product as a pale yellow solid (0.15 g, 52 %). Anal. Found: C, 49.2; H, 4.0; N, 16.9. $C_{17}H_{16}BN_4Pd \cdot 0.5H_2O$. Calc.: C, 49.0; H, 4.1; N, 16.8 %. ^1H NMR ($CDCl_3$) δ 8.23 (d, ^3J = 5.5 Hz, 1, $H6_{py}$), 7.59 (m, 4, H_{Phpy}) and 7.51 (d, 1, ^3J = 2.3 Hz, $H3_{pz}$) overlapping, 7.33 (m, 2, H_{Phpy} and $H3'_{pz}$ overlapping), 7.10 (m, 1, H_{Phpy}), 6.97 (m, 2, $H5,5'_{pz}$), 6.91 (m, 1, H_{Phpy}), 6.13 ('t', 1, $H4_{pz}$) and 6.10 ('t', 1, $H4'_{pz}$) overlapping. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 166.6, 155.4, 150.3 ($C6_{py}$), 146.4, 142.3, 140.1, 139.5, 136.4, 136.2, 135.6, 129.9, 125.4, 124.0, 122.6, 119.4, 106.0 (C4), 105.7 (C4′).

2.2. X-ray structure determination

Crystals of (**1**) and (**2**) formed at −30°C in dichloromethane/diethyl ether and at room temperature in dichloromethane/pentane solutions, respectively. For each complex, a unique data set was measured at 295 K using an Enraf–Nonius CAD-4 diffractometer operating in conventional 2θ–θ scan mode with monochromatic Mo Kα radiation (λ = 0.71073 Å), yielding N independent reflections, N_o with $I > 3\sigma(I)$ considered ob-

Table 3
Atom coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms of $Pd(C_6H_4C_5H_4\text{-}C,N)\{(pz)_3BH\text{-}N,N'\} \cdot 0.5\ Et_2O$ (**2**)

Atom	*x*	*y*	*z*	U_{eq}(Å^2)
Pd	0.20584(8)	0.34545(6)	0.51268(5)	0.0456(3)
N(1a)	0.4568(7)	0.2396(6)	0.5613(5)	0.047(4)
N(2a)	0.3900(7)	0.2893(6)	0.6004(5)	0.049(4)
C(3a)	0.467(1)	0.2955(8)	0.6872(6)	0.055(5)
C(4a)	0.588(1)	0.2519(8)	0.7064(7)	0.061(5)
C(5a)	0.5763(9)	0.2170(8)	0.6244(7)	0.056(5)
N(1b)	0.3745(7)	0.3325(6)	0.4150(5)	0.046(4)
N(2b)	0.2953(8)	0.3956(6)	0.4342(5)	0.051(4)
C(3b)	0.306(1)	0.4826(8)	0.4006(7)	0.061(6)
C(4b)	0.390(1)	0.4795(9)	0.3600(8)	0.074(6)
C(5b)	0.431(1)	0.3831(8)	0.3704(7)	0.060(5)
N(1c)	0.4805(7)	0.1644(6)	0.4262(5)	0.051(4)
N(2c)	0.6016(8)	0.1956(7)	0.4378(6)	0.066(5)
C(3c)	0.654(1)	0.1186(9)	0.4148(8)	0.074(6)
C(4c)	0.571(1)	0.0363(9)	0.3890(7)	0.075(6)
C(5c)	0.464(1)	0.0690(8)	0.3975(7)	0.060(5)
B	0.393(1)	0.2279(9)	0.4538(8)	0.045(5)
C(1d)	0.0276(9)	0.3932(7)	0.4328(6)	0.041(4)
C(2d)	−0.0676(9)	0.3707(7)	0.4614(6)	0.046(4)
C(3d)	−0.192(1)	0.3992(8)	0.4134(7)	0.058(5)
C(4d)	−0.228(1)	0.4539(8)	0.3363(8)	0.065(6)
C(5d)	−0.136(1)	0.4772(8)	0.3055(7)	0.066(6)
C(6d)	−0.009(1)	0.4478(8)	0.3537(7)	0.056(5)
N(1e)	0.1072(8)	0.2962(6)	0.5844(5)	0.056(4)
C(2e)	−0.0196(9)	0.3151(7)	0.5465(7)	0.047(5)
C(3e)	−0.096(1)	0.2828(8)	0.5900(7)	0.058(5)
C(4e)	−0.041(1)	0.2322(9)	0.6718(8)	0.073(6)
C(5e)	0.086(1)	0.215(1)	0.7081(7)	0.076(6)
C(6e)	0.159(1)	0.2450(9)	0.6635(7)	0.065(5)
C(02)[a]	−0.107(2)	0.082(1)	0.316(1)	0.045(5)
C(01)[a]	−0.009(2)	0.104(2)	0.366(1)	0.084(8)
O(0)[a]	0.021(2)	0.061(2)	0.445(2)	0.25(2)
C(01′)[a]	−0.032(4)	−0.039(2)	0.487(2)	0.16(2)
C(02′)[a]	−0.102(2)	−0.020(2)	0.566(1)	0.074(7)

[a] Site occupancy factor = 0.5.

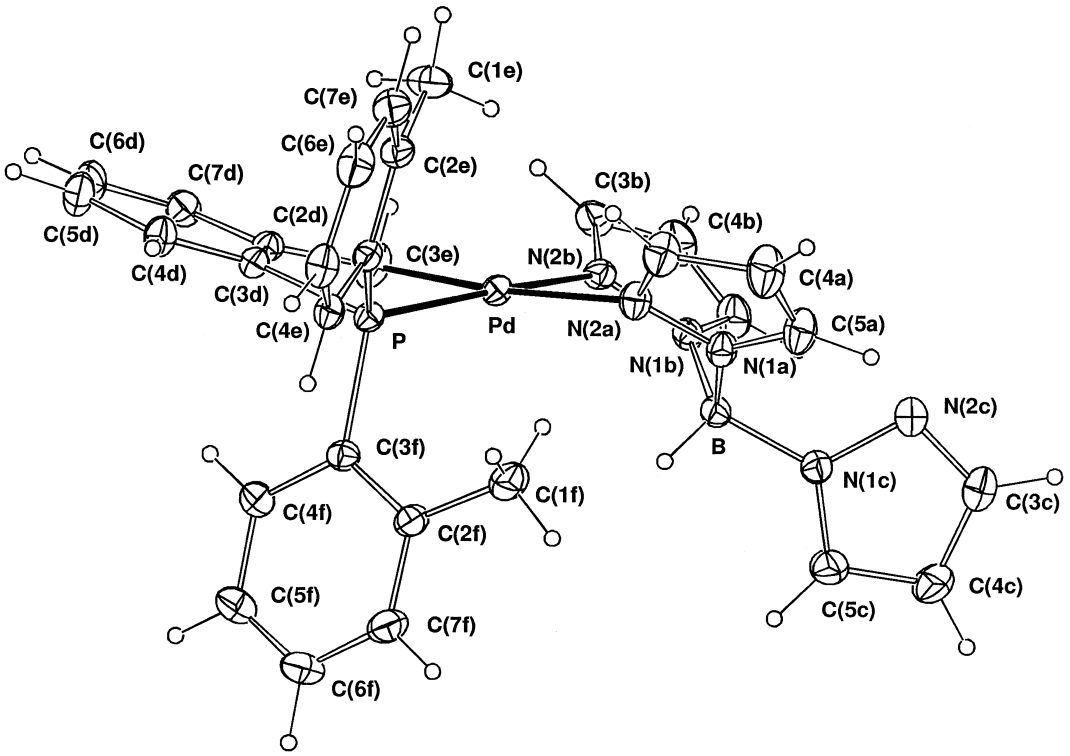


Fig. 1. The molecular structure of Pd{2-$CH_2C_6H_4P(o\text{-tol})_2$}{$(pz)_3BH$} (**1**). Thermal ellipsoids (20%) are shown for the non-hydrogen atoms, and hydrogen atoms have been given an arbitrary radius of 0.1 Å.

served and used in the full matrix least-squares refinement after Gaussian absorption correction and solution of the structures by vector methods. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms; $(x,\ y,\ z,\ U_{iso})_H$ were included constrained at estimated values. Residuals R and R_w are quoted or F at convergence; statistical weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ were employed. Neutral

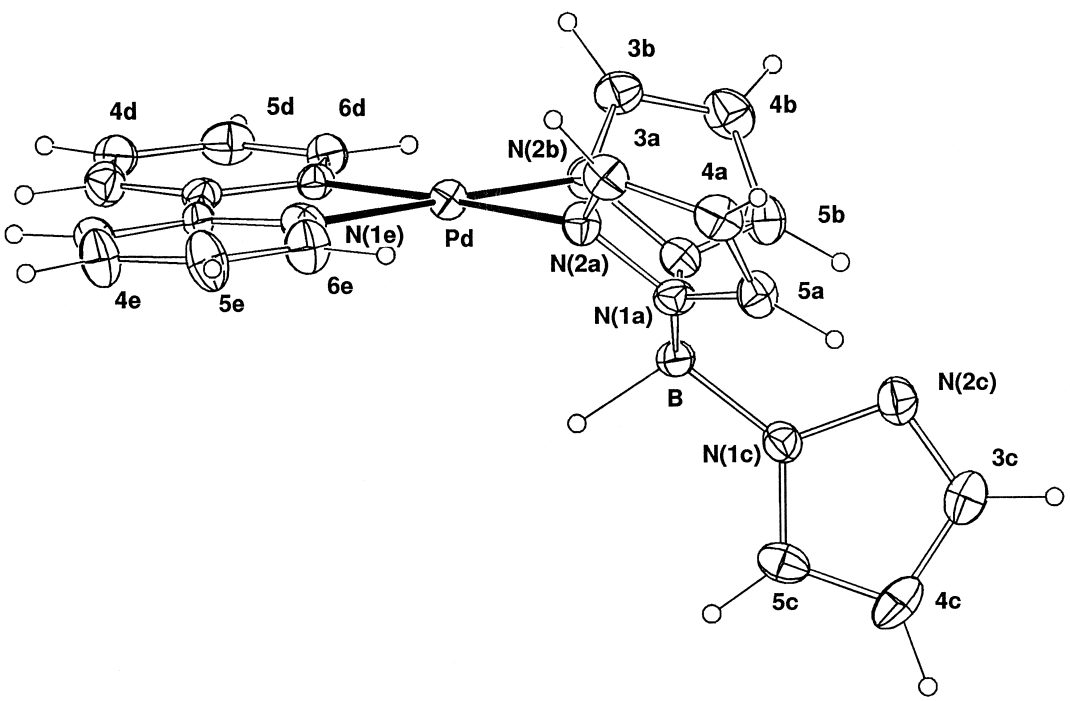


Fig. 2. Molecular structure of Pd($C_6H_4C_5H_4N$–C^2,N'){$(pz)_3BH$} (**2**).

atom complex scattering factors were used [25]; computation used the XTAL 3.0 program system implemented by Hall and Stewart [26]. Crystal data and selected geometries of the complexes are given in Tables 1–3, and views of the complexes are shown in Figs. 1 and 2.

In **2**, difference map residues were modelled as a diethyl ether molecule of solvation (C, O thermal parameters isotropic) disordered about an inversion centre. Assignment of coordinated nitrogen and carbon in the aromatic ligand was made on the basis of considerations of geometry and refinement behaviour.

2.3. In situ NMR reactions with electrophiles

In a typical reaction, the complex (0.015 mmol) was dissolved in acetone-d_6 (0.3 ml) or CD_2Cl_2 (0.3 ml) in a 5 mm NMR tube. The solution was cooled to −40°C and a stoichiometric amount of RX (RX = MeI, $PhCH_2Br$, PhI, 4-BrC_6H_4OMe) or halogen (Cl_2 as phenyliodonium dichloride, I_2) added. ^{1}H NMR spectra were recorded from −40°C to 0°C over a period of 1 h. In the case of RX addition, where no reaction was apparent, a further 9 equivalents were added and spectra recorded after 24 h at room temperature.

3. Results and discussion

3.1. Synthesis and characterization of complexes

Complexes **1**–**4** were prepared in moderate to high yield in acetone via halogen abstraction/bridge splitting reactions of cyclopalladated halide bridged precursors with the potassium salt of bis- or tris(pyrazol-1-yl)borate. All of the complexes are white or pale yellow, thermally stable, and stable in air and in solution, although slow decomposition occurred for **3** in chlorinated solvents. ^{1}H NMR spectra of complexes containing tris(pyrazol-1-yl)borate (**1** and **2**) exhibit one pyrazole environment at room temperature indicating rapid exchange involving all three pyrazole groups. Three pyrazole environments are observed upon cooling to ≈ −80°C. Complex **1**, containing the cyclometallated tris(*o*-tolyl)phosphine group, shows one sharp ^{31}P resonance at 40.0 ppm (acetone-d_6) at room temperature. However, the *o*-tolyl methyl resonances are coalesced as one broad signal at room temperature, and are well resolved into two singlets at −60°C (2.52 and 1.54 ppm). As the temperature is increased slightly, two distinct methyl environments are still present, although one of the methyl resonances broadens, probably due to increased motion of the tolyl group. Complexes **3** and **4** show two pyrazolyl environments in the ^{1}H NMR spectrum at room temperature, as expected, since it is the uncoordinated pyrazole group in complexes **1** and **2** which allows rapid isomerisation, presumably involving five-coordinate intermediates. Complex **3** exhibits a ^{31}P resonance at 39.7 ppm (acetone-d_6). The two methyl resonances are coalesced into one broad signal at room temperature, and are resolved into two singlets (2.72 and 2.08 ppm) at −40°C. In the ^{1}H NMR spectra of complexes **1** and **3**, containing the $[P–C]^-$ ligand, the methylene protons are not clearly enough resolved in CD_2Cl_2 to determine $^3J_{PH}$. However, resolution is sufficient in toluene-d_8 at 253 K to determine that $^3J_{PH} = 2.6$ Hz for **1** and 2.8 Hz for **3**, and $^2J_{HH} = 13.9$ Hz for **1** and 14.3 Hz for **3**. We note also that the large difference in chemical shift of the methyl resonances of **1** (0.98 ppm) and **3** (0.63 ppm) in CD_2Cl_2 decrease when the spectra are recorded in toluene-d_8, to 0.70 for **1** and 0.29 for **3**.

3.2. X-ray structural studies of *1* and *2*

The complexes have square-planar geometry for palladium (Table 4, Figs. 1 and 2), and the chelate angle for the {2-$CH_2C_6H_4P(o\text{-tol})_2$} ligand in **1** [82.4(1)°] is similar to that reported for the same ligand in [Pd{2-$CH_2C_6H_4P(o\text{-tol})_2$}($\mu$-I)]$_2$ [79.6(2)°] [27], [Pd{2-$CH_2C_6H_4P(o\text{-tol})_2$}($\mu$-$O_2CMe$)]$_2$ [82.3(2)°] [1], and Pd{2-$CH_2C_6H_4P(o\text{-tol})_2$}($O_2CMe$)($NEt_2H$) [82.42(6)°] [8], and similar to that for the $[C–N]^-$ ligand in **2** [79.7(4)°]. In **1**, the palladocycle is appreciably puckered [as an envelope, with Pd deviant (Table 4)]; torsion angles around the ring (from the Pd–P bond) are −15.7(1), 15.6(2), −4.8(4), −10.5(4) and 16.2(2)°; in **2**, the palladocycle and coordination plane are essentially co-planar.

The tris(pyrazol-1-yl)borate ligands are present as *N,N′*-bidentates, with Pd–N(2a) ~0.05 Å longer than Pd–N(2b) reflecting the stronger trans influence of the alkyl and aryl groups compared to the phosphorus and nitrogen donor groups of the $[C–P]^-$ and $[C–N]^-$ ligands. The uncoordinated pyrazole rings are 'equatorial' in both complexes, i.e., not positioned above the coordination plane in an 'axial' orientation. In contrast, to our knowledge previously reported square-planar d^8 complexes of palladium(II), [28–30] platinum(II), [31,32] gold(III), [33] and rhodium(I) [34] containing the tris(pyrazol-yl)borate ligand have the uncoordinated group axial (including a protonated pyrazole group in $[Rh(CO)_2\{(3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)B\text{-}N,N'\}]^+$) [35], except for $PtMe(CNBu^t)\{(pz)_3BH\}$ [36].

3.3. Reactivity of the complexes toward electrophiles

NMR spectroscopy (^{1}H, ^{31}P, acetone-d_6) was used to investigate the reactivity of the complexes reported herein toward electrophiles. None of the complexes studied react with methyl iodide, benzyl bromide, iodobenzene or 4-bromoanisole up to ambient temperature. Iodomethane and benzylbromide were examined because they readily form Pd(IV) complexes on oxida-

Table 4
Selected bond distances and angles for Pd{2-$CH_2C_6H_4P(o\text{-tol})_2$-*C,P*}-{$(pz)_3BH$-*N,N′*} (**1**) and Pd($C_6H_4C_5H_4N$-$C^2$,*N′*){$(pz)_3BH$-*N,N′*}·0.5$Et_2O$(**2**)

	(**1**)	(**2**)
Bond distances (Å)		
Pd–C(1d)	2.053(3)	1.995(9)
Pd–N(2a)	2.137(3)	2.113(7)
Pd–N(2b)	2.092(2)	2.05(1)
Pd–P, N(1e)	2.2325(9)	2.04(1)
C(3d)–P	1.813(3)	
C(2e)–N(1e)		1.33(1)
C(1d)–C(2d)	1.496(5)	1.38(2)
C(2d)–C(2e)		1.46(1)
C(2d)–C(3d)	1.383(4)	
B–N(a1)	1.545(5)	1.59(1)
B–N(b1)	1.554(4)	1.52(1)
B–N(c1)	1.513(4)	1.52(2)
Bond angles (°)		
C(1d)–Pd–P, N(1e)	82.4(1)	79.7(4)
C(1d)–Pd–N(2a)	173.4(1)	176.9(4).
C(1d)–Pd–N(2b)	89.2(1)	97.2(4)
N(2a)–Pd–N(2b)	86.3(1)	85.7(3)
N(2a)–Pd–P, N(1e)		97.3(3)
N(2b)–Pd–P, N(1e)	170.45(7)	176.8(3)
Pd–C(1d)–C(2d)	118.4(2)	116.0(6)
Pd–C(1d)–C(6d)		126.6(9)
Pd–P–C(3d)	104.3(1)	
Pd–P–C(3e)	122.8(1)	
Pd–P–C(3f)	111.9(1)	
Pd–N(1e)–C(2e)		115.2(7)
Pd–N(1e)–C(6e)		125.9(8)
Pd–N(2a)–N(1a)	120.1(2)	117.1(5)
Pd–N(2a)–C(3a)	132.0(2)	136.2(8)
Pd–N(2b)–N(1b)	120.7(2)	118.9(6)
Pd–N(2b)–C(3b)	132.5(2)	135.0(9)
C(1d)–C(2d)–C(3d)	118.8(3)	
C(1d)–C(2d)–C(2e)		113.5(8)
C(2d)–C(3d)–P	112.6(2)	
C(2d)–C(2e)–N(1e)		116(1)
N(a1)–B–N(b1)	107.7(3)	106.2(8)
N(a1)–B–N(c1)	112.5(3)	109.1(7)
N(b1)–B–N(c1)	110.0(3)	113(1)
Deviations from 'PdCN$_2$P' and 'PdCN$_3$' coordination mean planes (Å)[a]		
Pd	0.013(1)	−0.001(1)
C(1d)	0.129(4)	0.02(1)
P, N(1e)	−0.015(1)	0.02(1)
C(2d)	0.511(4)	0.06(1)
C(3d)	0.555(4)	
C(2e)		0.07(1)
N(2a)	0.061(4)	0.02(1)
N(2b)	−0.108(3)	0.02(1)
Deviations from palladocycle mean planes 'C$_3$P' and 'PdC$_3$N'[b]		
Pd	0.478(4)	0.000(1)
C(1d)	0.017(5)	0.01(1)
C(2d)	−0.027(4)	0.00(1)
C(3d), C(2e)	0.024(4)	−0.01(1)
P, N(1e)	−0.001(1)	0.01(1)
Deviations from pyrazole 'C$_3$N$_2$' mean planes (Å)[c]		
Pd (ring a)	0.301(6)	0.19(2)
Pd (ring b)	0.172(6)	0.17(2)
B (ring a)	−0.014(6)	0.13(2)
B (ring b)	0.051(6)	0.14(2)
B (ring c)	0.049(6)	0.13(2)
Angles between mean planes		
Coord/palladocycle	19.0(1)	1.2(2)
Coord/a	44.3(1)	48.9(4)
Coord/b	38.7(1)	50.3(4)
Coord/c	85.5(1)	77.8(4)
Palladocycle/ring a	43.2(1)	49.6(4)
Palladocycle/ring b	21.4(1)	50.9(4)
Palladocycle/ring c	89.0(1)	77.8(4)
Rings a/b	58.7(2)	75.3(5)
Rings a/c	48.7(2)	63.6(5)
Rings b/c	72.8(2)	41.8(5)

[a] χ^2 values for 'PdCN$_2$P,' 'PdCN$_3$' mean plane are 2915 and 12, respectively.
[b] χ^2 values for palladocycles 'C$_3$P' and 'PdC$_3$N' are 99 and 3, respectively.
[c] χ^2 values for pyrazole mean planes a, b, and c are 1.3, 8.0, 2.2, and 1.2, 0.0, 0.2, respectively.

tive addition to diorganopalladium(II) complexes and 4-bromoanisole because of its successful application in syntheses using [Pd{2-$CH_2C_6H_4P(o\text{-tol})_2$}($\mu$-$O_2CMe$)]$_2$ as a catalyst [1–6]. All of the complexes decompose to dark suspensions in the presence of iodine or phenyliodonium dichloride ($PhICl_2$), a reagent used to deliver chlorine stoichiometrically. The complex [Pd{2-$CH_2C_6H_4P(o\text{-tol})_2$}($\mu$-$O_2CMe$)]$_2$ was also found to be unreactive toward iodobenzene and 4-bromoanisole, although the absence of oxidative addition in these reactions does not preclude its occurrence under the different conditions used in studies involving this complex as a catalyst. However, to date there are no documented examples of oxidative addition of aryl halides to palladium(II), and even for more reactive platinum(II) substrates oxidative addition appears to be limited to the more favourable situation where the aryl–halogen bond is part of an intramolecularly coordinated ligand [37–42].

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