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C–H activation at the 3-position of pentane chains to form $[N–C(sp^3)–N]^-$ complexes incorporating six-membered pallada(II)cyclic rings and pyridine, pyrazole and *N*-methylimidazole donor groups. Structural studies and comparison with $[N–C(sp^2)–N]^-$ complexes

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Dedicated to Professor Martin Bennett on the occasion of his retirement.

Abstract

Alkylpalladium complexes bearing the $[N–C(sp^3)–N]^-$ donor motif and two six-membered palladacycles are generated on activation of $C(sp^3)$–H bonds by palladium(II) acetate. Cyclopalladation of the new reagents 1,5-bis(pyridin-2-yl)pentane $[CH_2(CH_2CH_2py)_2]$ (**1**), 1,5-bis(pyrazol-1-yl)pentane $[CH_2(CH_2CH_2pz)_2]$ (**2**) and 1,5-bis(*N*-methylimidazol-2-yl)pentane $[CH_2(CH_2CH_2mim)_2]$ (**3**), followed by reaction with lithium chloride afford the palladium(II) complexes Pd{$CH(CH_2CH_2py)_2$-*N*,*C*,*N*′}Cl (**5**), Pd{$CH(CH_2CH_2pz)_2$-*N*,*C*,*N*′}Cl (**6**) and Pd{$CH(CH_2CH_2mim)_2$-*N*,*C*,*N*′}Cl (**7**), respectively. Abstraction of chloride from **6** with $AgBF_4$ in acetone generates the cationic acetone complex [Pd{$CH(CH_2CH_2pz)_2$-*N*,*C*,*N*′}$(OCMe_2)$][BF_4] (**8**). X-ray crystal structures of **5**, **6** and **8** reveal tridentate $[N–C(sp^3)–N']^-$ intramolecular coordination of the ligands. These structures are compared with that of a closely related $[N–C(sp^2)–N]^-$ system in [Pd{2,6-$(pzCH_2)_2C_6H_3$-*N*,*C*,*N*′}(OH_2)][BF_4] (**10**), obtained on cyclopalladation of 1,3-bis(pyrazol-1-ylmethyl)benzene followed by derivatisation to form the aqua complex.

Keywords: Organopalladium; Intramolecular coordination; Cyclometallation; Crystal structure

1. Introduction

Intramolecular coordination systems with the symmetrical donor motif $[E–C–E]^-$ (E = donor element) coordinated to palladium(II) have attracted considerable interest, but there are few examples where the central carbon atom is an aliphatic sp^3 centre (**I**–**III**) [1–4]. Only one of these is a six-membered $[E–C(sp^3)–E]^-$ system (**III**) [4], and for aryl systems $[E–C(sp^2)–E]^-$ this ring size is also rare (**IV** and **V**) [5–8]. Complexes **I**–**V** have been synthesised via cyclopalladation reactions. We report here an investigation of the applicability of the cyclopalladation strategy for the synthesis of relatives of **II** containing six-membered chelate rings using the reagents $CH_2(CH_2CH_2X)_2$ [X = pyridin-2-yl (py), pyrazol-1-yl (pz) and *N*-methylimidazol-2-yl (mim)], resulting in the synthesis of $[N–C(sp^3)–N]^-$ systems of type **VI**. The new systems contain nitrogen donor groups with different donor abilities (mim > py > pz) [9], but providing similar coordination geometries for the $[E–C(sp^3)–E]^-$ unit.

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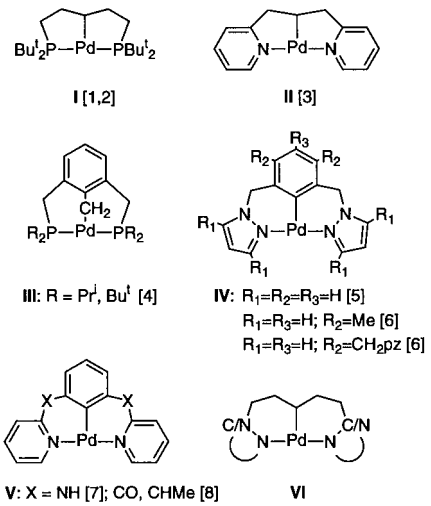

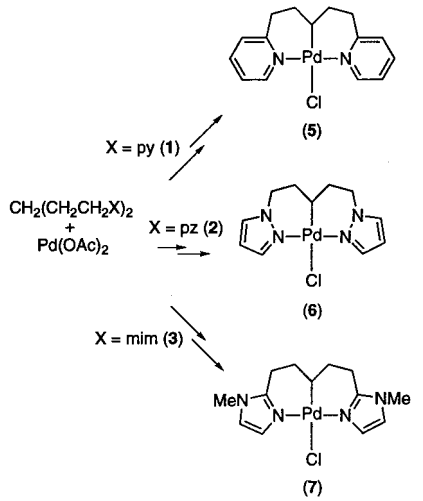

Scheme 1.

2. Results and discussion

2.1. Synthesis and characterisation of complexes

The compounds $CH_2(CH_2CH_2X)_2$ (X = py, pz, mim) were obtained on reaction of dibromoalkanes with alkali metal reagents. Thus, 1,5-bis(pyridin-2-yl)pentane (**1**) was prepared by treating a solution of 2-picolyllithium with half an equivalent of 1,3-dibromopropane, following a procedure used by Brzezinski and Zundel for the synthesis of other bis(pyridin-2-yl)alkanes [10]. The pyrazole analogue, 1,5-bis(pyrazol-1-yl)pentane (**2**), was generated on refluxing a mixture of pyrazol-1-ylpotassium and half an equivalent of 1,5-dibromopentane in tetrahydrofuran. Similarly, 1,5-bis(*N*-methylimidazol-2-yl)-pentane (**3**) formed on addition of *N*-methylimidazol-2-yllithium to half an equivalent of 1,5-dibromopentane.

Cyclometallated complexes **5**–**7** were found to be generated on reaction of **1**–**3** with one equivalent of palladium acetate in refluxing acetic acid, and isolated as chloro complexes after reaction with lithium chloride (Scheme 1). The best yields (12–35%) were obtained after long reaction times (~ 12 h), and after this time the major by-products detected were found to be the free ligand and palladium(0). Isolation of the complexes in low yield could result from several factors, including palladation of other sites in the ligand followed by decomposition. Thus, when 1,5-bis(pyrazol-1-yl)pentane (**2**) and one equivalent of palladium acetate were refluxed in acetic acid-d_4 for 12 h, ^{1}H-NMR analysis of the product indicated deuterium incorporation into the 3, 4 and 5 positions of the pyrazole rings while no deuterium incorporation into the alkyl chain was observed. When 1,5-bis(pyrazol-1-yl)pentane was treated under the same conditions in the absence of palladium acetate no deuterium incorporation was observed. However, for 1,5-bis(pyridin-2-yl)pentane (**1**) deuterium was incorporated at one methylene group, $(pyCHDCH_2)CH_2$, and no incorporation occurred in the absence of palladium acetate. Insoluble decomposition products formed in an analogous experiment for 1,5-bis(*N*-methylimidazol-2-yl)pentane (**3**), and in the absence of palladium acetate no deuterium incorporation was detected.

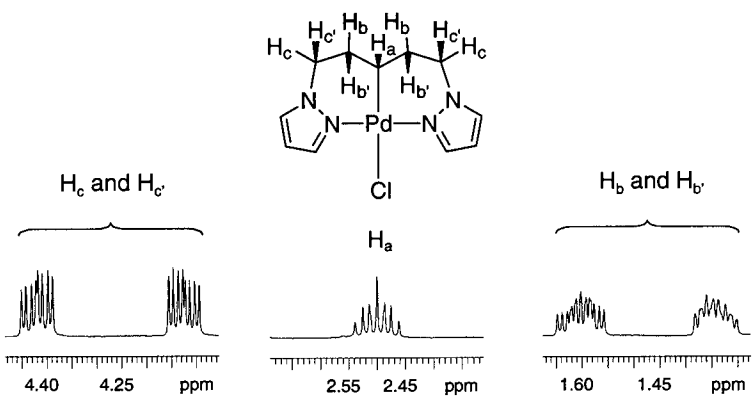

Fig. 1. Alkyl region of the ^{1}H-NMR spectrum for Pd{CH(CH$_2$CH$_2$pz)$_2$-*N*,*C*,*N*′}Cl (**6**).

Table 1
Specific crystallographic details for Pd{CH(CH$_2$CH$_2$py)$_2$-*N*,*C*,*N*′}Cl (**5**), Pd{CH(CH$_2$CH$_2$pz)$_2$-*N*,*C*,*N*′}Cl (**6**), [Pd{CH(CH$_2$CH$_2$pz)$_2$-*N*,*C*,*N*′}(OCMe$_2$)][BF$_4$] (**8**), and [Pd{2,6-(pzCH$_2$)$_2$C$_6$H$_3$-*N*,*C*,*N*′}(OH$_2$)][BF$_4$] (**10**)

Complex	**5**	**6**	**8**	**10**
Formula	$C_{15}H_{16}ClN_2Pd$	$C_{11}H_{15}ClN_4Pd$	$C_{14}H_{20}BF_4N_4OPd$	$C_{14}H_{15}BF_4N_4OPd$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/a$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a (Å)	11.447(3)	17.166(4)	9.152(2)	7.859(1)
b (Å)	8.825(2)	8.744(3)	24.53(1)	14.441(4)
c (Å)	14.219(8)	8.486(3)	8.188(5)	14.895(5)
β (°)	96.57(3)	90.32(2)	101.20(3)	99.51(2)
V (Å^3)	1427	1274	1803	1667
Z	4	4	4	4
M_r	366.2	345.1	453.6	448.5
D_{calc} (g cm^{-3})	1.70_4	1.80_0	1.67_0	1.78_2
μ_{Mo} (cm^{-1})	14.7	16.5	10.8	11.6
$F(000)$	732	688	908	888
Specimen (mm)	$0.28 \times 0.35 \times 0.80$	$0.28 \times 0.28 \times 0.10$	$0.50 \times 0.14 \times 0.45$	$0.75 \times 0.18 \times 0.14$
$2\theta_{max}$ (°)	55	55	50	56
$A^*_{min,\ max}$	1.18, 1.62	1.16, 1.55	1.16, 1.57	1.19, 1.25
n_v	174	174	244	240
$\lvert\Delta\rho_{max}\rvert$ (e Å^{-3})	1.7	1.6	1.0	0.5
N, N_0	3274, 2279	3694, 2552	3157, 1915	4017, 3062
R, R_w	0.050, 0.062	0.049, 0.058	0.057, 0.066	0.037, 0.039

The complexes **5**, **6** and **7** were characterised by microanalysis and ^{1}H-,^{13}C-, COSY and HETCOR NMR spectroscopy. A single set of ^{1}H- and ^{13}C-NMR resonances for the *N*-heterocyclic donor groups for each complex indicated the equivalence of the *trans* donor groups. The methine proton resonances (2.2–2.6 ppm) occur at similar chemical shifts to the methine resonance observed for the methylpalladium(II) complex containing the [P–C(sp^3)–P]$^-$ system in **I** (2.22 ppm) [2]. The methine resonance for each complex appears as a triplet of triplets due to coupling with the two pairs of protons H$_b$ and H$_{b'}$ (Fig. 1). For complexes **5** and **6** the ^3J coupling constants could not be determined due to overlapping resonances, however values of 3.0 and 10.5 Hz were determined for **7**.

The resonances for the two pairs of methylene protons H$_c$ and H$_{c'}$ each appear as a doublet of doublets of doublets. The resonances were best resolved for complex **6** (Fig. 1) for which one pair exhibits $^3J = 3.2$, 8.2 Hz and $^2J = 13.2$ Hz, and the other pair $^3J = 3.6$, 8.0 Hz and $^2J = 13.4$ Hz. The similarity between the coupling constants for H$_c$ and H$_{c'}$ suggest that a rapid inversion process occurs, since significant differences between the ^3J coupling constants for each pair would be expected in a rigid system due to different dihedral angles. The inversion process is still evident at low temperature with no apparent change in the ^{1}H-NMR spectra for **6** between -50 and 50°C. As a result of this inversion, through space interactions are inherently difficult to interpret, so that methylene resonances can only be assigned as either H$_b$ or H$_{b'}$, or H$_c$ or H$_{c'}$ (Fig. 1). In the structurally related complex, Pd{3,5-Me$_2$-2,6-(pzCH$_2$)$_2$C$_6$H-*N*,*C*,*N*′}Cl (**V**: R$_1$ = R$_3$ = H, R$_2$ = Me) [6], the fused six-membered palladacycles each exist in a boat conformation and invert rapidly at room temperature. This results in a single CH$_2$ resonance in the ^{1}H-NMR spectrum, which splits into two resonances on cooling as the inversion process slows. In complex **6**, although a similar inversion process occurs, the two sets of protons H$_c$ and H$_{c'}$ each resonate at a different frequency due to the lack of C_2 symmetry within the molecule.

In order to allow a comparison of structural data for the [N–C(sp^3)–N]$^-$ systems in **5**, **6** and **8** (see below) with a [N–C(sp^2)–N]$^-$ system, the complex Pd{2,6-(pzCH$_2$)$_2$C$_6$H$_3$-*N*,*C*,*N*′}Cl (**9**) was synthesised from the reported complex [Pd{2,6-(pzCH$_2$)$_2$C$_6$H$_3$-*N*,*C*,*N*′}(O$_2$CMe) [5]. However, this complex was not sufficiently crystalline for structural analysis, and was subsequently converted to the crystalline aqua derivative [Pd{2,6-(pzCH$_2$)$_2$C$_6$H$_3$-*N*,*C*,*N*′}(OH$_2$)}][BF$_4$] (**10**). Although the chloro complex may be readily obtained from the acetato complex following procedures developed for **5**–**7**, we report here an alternative synthesis via the isolation of PdCl$_2${1,3-(pzCH$_2$)$_2$C$_6$H$_4$}, followed by heating of this complex to form **10**. Thermogravimetric analysis of the latter process indicates a weight loss of 10%, close to that calculated for loss of HCl (8.8%).

2.2. X-ray structural studies

To date there are no examples of X-ray crystal structures of cyclopalladated, anionic [N–C(sp^3)–N]$^-$

units. Thus, X-ray crystal structures were determined for complexes **5**, **6**, **8** (a derivative of **6** in an attempt to obtain a structure for the [pz–C(sp^3)–pz]$^-$ kernel free of disorder). Crystals of **5** and **6** suitable for single crystal X-ray structure determinations were grown from dichloromethane–petroleum ether (b.p. 60–80°C) and chloroform–petroleum ether (b.p. 60–80°C) solutions, respectively; crystals of **10** were obtained on diffusion of diethyl ether into a solution of the complex in acetone. Pertinent results of structure determinations are quoted in Tables 1 and 2 and Figs. 1 and 2, the remainder being deposited.

In each of the four crystalline arrays, one formula unit devoid of crystallographic symmetry comprises the asymmetric unit of the structure, the arrays for **5** and **6** being neutral molecular complexes, unsolvated, and for **8** and **10** ionic complexes incorporating solvent in the coordination sphere of the metal, rather than the poorly coordinating anion. Not surprisingly, the quasi-spherical anions in **8** and **10** are disordered. Disorder is resolved for the hydrocarbon string of the ligand in **6**, while the large displacement amplitudes therein in **7**, may be presumed to indicate unresolved disorder. Associated geometries for these systems should be treated with caution.

The complexes have square planar geometry for palladium (Table 2, Figs. 2 and 3). For both [N–C(sp^3)–N]$^-$ and [N–C(sp^2)–N]$^-$ units, C–Pd–N angles at palladium are close to 90°. These angles are within ca. 1° of 90° for the [N–C(sp^2)–N]$^-$ complex **10** and the reported complex PdCl{3,5-Me$_2$-2,6-(pzCH$_2$)$_2$C$_6$H-*N*,*C*,*N*′} [6], and within ca. 3° of 90° for the [N–C(sp^3)–N]$^-$ pyrazole donor system in **8**; the related platinum(II) complex PtBr{2,6-(3,5-Me$_2$pzCH$_2$)$_2$C$_6$H$_3$-*N*,*C*,*N*′} has C–Pt–N angles of 85.4(4) and 88.6(4)° [11].

The Pd–O(2) distance in the acetone complex **8**, 2.263(6) Å, longer than in the cyclopalladated azobenzene complex Pd(C$_6$H$_4$N=NPh-*C*,*N*)(PPh$_3$)(OCMe$_2$), 2.141(5) [12], and the Pd–O distance in the aqua complex **10**, 2.200(3) Å, is similar to that in other organopalladium(II) complexes containing the aqua ligand trans to an sp^3 carbon, 2.124(2) Å [13], or an sp^2 carbon, 2.20(1) [14] and 2.132(3) Å [15], but longer than in an organopalladium(IV) complex where the aqua ligand is opposite a pyrazole donor which has a weaker trans influence than an alkyl or aryl group, 2.035(4) Å [16].

For the coordination mean planes, the donor atoms are within 0.32(1) Å of the mean planes for **5**, **6** and **10** and the palladium atoms are within 0.070(3) Å for these complexes; the acetone complex (**8**) exhibits larger deviations [−0.08(1)–0.29(2) Å] for the donor atoms and 0.075(3) Å for the palladium atom (Table 2). The mean planes of nitrogen donor rings form dihedral angles with the coordination plane ranging from 14.2(4)–45.4(2)°, and the aryl ring bonded to palladium in **10** forms an angle of 36.2(1)° with the coordination plane. The six-membered ring conformations in **5** and **10** are quasi-boats, Pd and CH$_2$ at the prows, the two rings in each complex being related by a putative 2-axis through Pd–C(0), this symmetry and conformation carrying through rather less exactly to the counterpart arrays of **6** and **8** where overt or covert disorder is prevalent.

3. Conclusions

Organopalladium(II) complexes containing symmetrical [N–C(sp^3)–N]$^-$ intramolecular coordination systems with six-membered pallada(II)cyclic rings are readily formed on C(sp^3)–H activation of simple reagents (XCH$_2$CH$_2$)$_2$CH for a range of heterocyclic groups X = pyridin-2-yl, pyrazol-1-yl, *N*-methylimidazol-2-yl. The organic reagents are readily accessed via reactions of alkali metal reagents with dibromoalkanes, and thus offer interesting routes to studies in cyclometallation chemistry involving alkyl C–H activation.

4. Experimental

2-Picolyllithium [18] was prepared as described [17]. Solvents were dried and distilled, stored under nitrogen and freshly distilled immediately before use, and all procedures were carried out under nitrogen.

NMR spectra were recorded with either a Varian Unity Inova 400 WB spectrometer operating at 100.587 (^{13}C), 399.716 (^{1}H) MHz, or a Varian Gemini 200 spectrometer operating at 50.29 (^{13}C), 199.975 (^{1}H) MHz, at room temperature unless otherwise indicated. Chemical shifts are given in parts per million relative to SiMe$_4$.

Microanalyses were determined by the Central Science Laboratory, University of Tasmania.

4.1. Synthesis of reagents

4.1.1. 1,5-Bis(pyridin-2-yl)pentane (1)

To a stirred solution of 2-picolyllithium (30 mmol, 1 M solution in diethyl ether) was added, dropwise over 1 h, a solution of 1,3-dibromopropane (10 mmol) in diethyl ether (20 ml). The mixture was stirred for 3 h, then hydrolysed by the dropwise addition of water (50 ml). The aqueous layer was separated and extracted with dichloromethane (3 × 20 ml), and the organic fraction dried over MgSO$_4$, filtered, and evaporated to dryness in a vacuum. The product was purified by bulb-to-bulb distillation (1.45 g, 64%). B.p.: (140°C, 0.08 Torr). ^{1}H-NMR (CDCl$_3$, 200 MHz): δ 8.50 (dd, $^3J = 4.9$, $^5J = 1.8$ Hz, 2, *H*6), 7.58 (m, 2, *H*4), 7.12–7.04

Table 2
Selected molecular geometries for Pd{CH(CH_2CH_2py)$_2$-*N,C,N′*}Cl (**5**), Pd{CH(CH_2CH_2pz)$_2$-*N,C,N′*}Cl (**6**), [Pd{CH(CH_2CH_2pz)$_2$-*N,C,N′*}($OCMe_2$)][BF_4] (**8**), and [Pd{2,6-($pzCH_2$)$_2$$C_6H_3$-*N,C,N′*}($OH_2$)][$BF_4$] (**10**) [a]

	5	**6**	**8**	**10**
Distances (Å)				
Pd–X	2.457(2)	2.463(2)	2.263(6)	2.200(3)
Pd–C(0)	2.050(8)	1.99(1), 2.086(9)	2.01(1)	1.973(4)
Pd–N(11)	2.058(4)	2.032(4)	2.045(8)	2.008(3)
Pd–N(21)	2.060(5)	2.032(4)	2.027(9)	2.021(3)
Angles (°)				
X–Pd–C(0)	175.0(3)	173.8(4), 169.1(3)	173.4(4)	177.7(1)
X–Pd–N(11)	90.9(1)	91.7(1)	91.8(1)	88.3(1)
X–Pd–N(21)	92.5(1)	88.9(1)	85.1(3)	92.7(1)
C(0)–Pd–N(11)	85.6(3)	85.6(4), 93.6(3)	92.5(5)	89.7(1)
C(0)–Pd–N(21)	90.9(3)	94.1(4), 85.5(3)	91.4(5)	89.3(1)
N(11)–Pd–N(21)	176.3(2)	177.9(2)	171.1(3)	178.6(1)
Pd–N(11)–C/N(12)	122.2(4)	126.5(3)	127.6(7)	122.6(2)
Pd–N(11)–C(15/16)	118.6(4)	128.1(4)	126.1(6)	131.5(3)
Pd–N(21)–C/N(22)	121.4(4)	123.0(3)	128.5(7)	121.7(3)
Pd–N(21)–C(25/26)	119.9(4)	130.2(4)	126.6(8)	131.6(3)
Pd–C(0)–C(122)	113.9(5)	118.2(8), 112.9(6)	116(1)	120.1(3)
Pd–C(0)–C(222)	119.0(5)	118.4(8), 114.3(6)	116(1)	120.5(3)
Pd–O(2)–C(2)	–	–	124.9(5)	–
Plane parameters (χ^2, *atom deviations* δ Å)				
χ^2(X,C(0), N(11,21))(1)	34	227, 372	361*	82
δPd	0.038(2)	0.015(3), 0.070(3)	0.075(3)	0.002(1)
χ^2(N(11)–C(15/16))(2)	9	0.9	0.8	2.4
δPd	0.009(8)	0.137(10)	0.36(2)	0.070(7)
χ^2(N(21)–C(15/16))(3)	18	1.3	0.2	14
δPd	0.054(8)	0.295(9)	0.14(2)	0.206(7)
Other atom deviations from the X, C(0) *N*(11,21) *plane*:				
δPd	0.038(2)	−0.015(3), −0.070(3)	−0.075(3)	0.001(1)
δN/C(12)	0.797(9)	0.507(8), 0.426(8)	0.29(2)	0.640(5)
δC(15/16)	−0.844(8)	−0.321(9), −0.353(9)	0.022(1)	−0.572(6)
δN/C(22)	−0.739(8)	−0.497(8), −0.575(8)	−0.24(2)	−0.638(6)
δC(25/26)	0.728(8)	0.679(8), 0.645(7)	0.64(2)	0.737(6)
δC(121)	1.697(9)	0.60(2)/1.28(1), 0.48(2)/1.17(1)	0.17(2)	1.460(6)
δC(122)	0.959(9)	0.58(1), 0.46(1)	−0.21(3)	0.670(6)
δC(221)	−1.468(9)	−1.315(10), −1.418(10)	−0.75(3)	−1.504(6)
δC(222)	−0.524(9)	−0.59(1), −0.71(1)	−0.62(3)	−0.738(6)
δC(0',0)	−0.06(1)	−0.22(1), 0.31(2)	−0.29(2)	−0.027(5)
δX	−0.002(2)	−0.003(2), 0.005(2)	0.037(7)	−0.017(4)
δN(11)	0.012(6)	0.022(6), −0.034(6)	0.07(1)	0.017(4)
δN(21')	0.011(6)	0.019(6), −0.035(6)	0.08(1)	0.018(4)
Interplanar dihedral angles (°)				
(1)/(2)	45.4(2)	23.6(2), 22.2(2)	14.2(4)	34.3(1)
(1)/(3)	40.2(2)	34.3(2), 35.6(2)	26.2(5)	40.2(2)
(2)/(3)	85.6(2)	57.8(3)	34.1(6)	73.8(2)
Torsion angles (°)				
C(0)–Pd–N(11)–C/N(12)	−46.9(5)	−31.8(6)	−15.3(8)	−33.6(3)
C(0)–Pd–N(21)–C/N(22)	−37.7(5)	−21.8(6)	15.7(10)	−34.3(3)
Pd–N(11)–C/N(12)–C(121)	−0.4(7)	25(1), −10(1)	15(1)	−7.1(5)
Pd–N(21)–C/N(22)–C(221)	5.0(7)	−12(7)	1(2)	−7.6(5)
N(11)–C/N(12)–C(121)–C(222)	58.6(7)	−20(2), 54(1)	0(2)	56.1(5)
N(21)–C/N(22)–C(221)–C(222)	55.9(7)	60.3(7)	18(3)	57.8(5)
C/N(12)–C(121)–C(122)–C(0)	−49.6(8)	36(2), −41	−16(4)	−53.1(5)
C/N(22)–C(221)–C(222)–C(0)	−74.1(7)	−67(1), −40(1)	−16(4)	−54.3(5)
C(121)–C(122)–C(0)–Pd	−14.7(9)	(?)	11(4)	0.4(5)
C(221)–C(222)–C(0)–Pd	26.7(9)	25(1), −20(1)	−6(3)	−0.1(5)
C(121)–C(122)–C(0)–C(222)	−164.3(6)	(?)	−175(3)	−179.7(3)
C(221)–C(222)–C(0)–C(122)	174.7(6)	175(1), −156.9(8)	180(3)	180.0(4)
N(11)–Pd–C(0)–C(122)	51.1(6)	41.6(9), 5.9(8)	4(2)	35.5(3)
N(11)–Pd–C(0)–C(222)	−159.2(7)	−168.4(1), −132.8(7)	−171(1)	−144.4(3)
N(21)–Pd–C(0)–C(122)	−130.2(6)	−136.3(9), −172.2(8)	−168(2)	−143.5(3)
N(21)–Pd–C(0)–C(222)	19.5(7)	13.7(9), 49.1(7)	17(1)	36.6(3)

[a] For the acetone skeleton, χ^2 is 2,4, δPd 0.59(2) Å, and the dihedral to N_2CO 74.6(4)°. The distance between the C(0,0′) components in **6** is 0.62(2) Å; where two entries are given, these are for the two disordered arrays; certain of the torsion angles are determined by more than one component and, having some ambiguity, are denoted (?). In **10** the dihedral angles for the coordinated C_6 ring to the planes 1–3 are 36.2(1), 49.8(2) and 56.6(2)°.

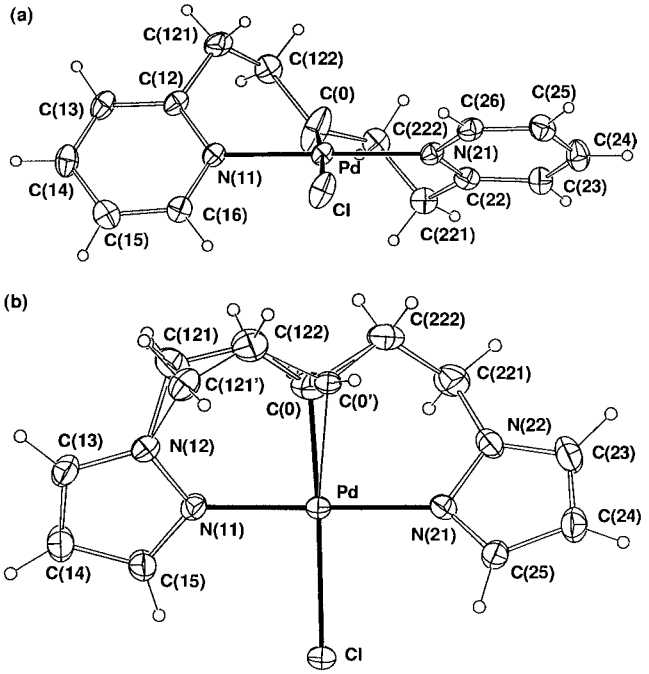

Fig. 2. Projection of (a) a molecule of Pd{CH(CH_2CH_2py)$_2$-*N*,*C*,*N*′}Cl (**5**), and (b) a molecule of Pd{CH(CH_2CH_2pz)$_2$-*N*,*C*,*N*′}Cl (**6**) illustrating disorder in the latter complex. The projections show 20% thermal ellipsoids for the non-hydrogen atoms, hydrogen atoms having an arbitrary radius of 0.1 Å.

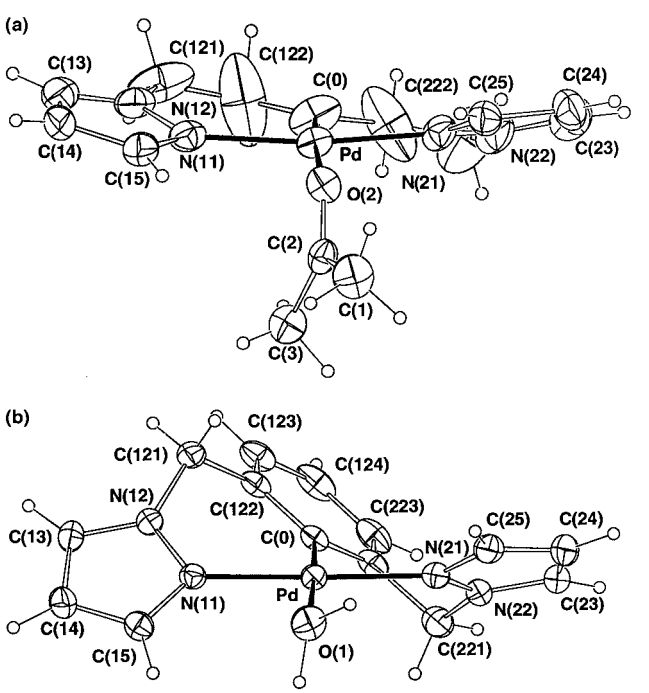

Fig. 3. Projection of the cation in (a) [Pd{CH(CH_2CH_2pz)$_2$-*N*,*C*,*N*′}(OMe$_2$)][BF_4] (**8**), and (b) [Pd{2,6-(pzCH_2)C_6H_3-*N*,*C*,*N*′}(OH_2)][BF_4] (**10**). The projections show 20% thermal ellipsoids for the non-hydrogen atoms, hydrogen atoms having an arbitrary radius of 0.1 Å.

(m, 4, *H*3,5), 2.77 (t, $^3J = 7.8$ Hz, 4, py CH_2), 1.77 (m, 4, pyCH_2CH_2), 1.42 (m, 2, py$CH_2CH_2CH_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 50 MHz): δ 162.8 (*C*6), 149.7 (*C*2), 136.7 (*C*4), 123.2 (*C*3), 121.4 (*C*5), 38.8 (pyCH_2), 30.2 (pyCH_2CH_2), 29.6 (py$CH_2CH_2CH_2$). Anal. Calc. for $C_{15}H_{20}N_2$: C, 79.61; H, 8.01; N, 12.38. Found: C, 79.59; H, 8.24; N, 12.24%.

*4.1.2. 1,5-Bis(pyrazol-1-yl)pentane (**2**)*

To a stirred suspension of finely cut potassium (0.94 g, 24 mmol) in tetrahydrofuran (30 ml) was added pyrazole (1.70 g, 25 mmol). The mixture was heated to reflux and maintained at this temperature until beads of molten potassium were no longer evident ($\sim$90 min). The solution was cooled and 1,5-dibromopentane (10 mmol) added. The solution was refluxed for 8 h, then filtered and the solvent removed in a vacuum leaving a pale yellow oil. The product was purified by bulb-to-bulb distillation (135°C, 0.1 Torr). Yield: 79%. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.45 (d, $^3J = 1.80$ Hz, 2, *H*3), 7.29 (d, $^3J = 2.28$ Hz, 2, *H*5), 6.18 ('t', 2, *H*4), 4.06 (t, $^3J = 7.01$ Hz, 4, pzCH_2), 1.84 (q, $^3J = 7.40$ Hz, 4, pzCH_2CH_2), 1.22 (m, 2, pz$CH_2CH_2CH_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 50 MHz): δ 139.6 (*C*3), 129.4 (*C*5), 105.7 (*C*4), 52.2 (pzCH_2), 30.4 (pzCH_2CH_2), 24.1 (pz$CH_2CH_2CH_2$). Anal. Calc. for $C_{11}H_{16}N_4$: C, 64.68; H, 7.90; N, 27.43. Found: C, 64.51; H, 7.98; N, 27.48%.

*4.1.3. 1,5-Bis(N-methylimidazol-2-yl)pentane (**3**)*

To a stirred suspension of *N*-methylimidazole (3.16 g, 38.5 mmol) in diethyl ether (20 ml) at -70°C was added *n*-butyllithium (16.1 ml of 2.4 M, 38.5 mmol). The mixture was allowed to warm to -10°C and maintained at this temperature for 30 min. The mixture (a white suspension) was cooled to -70°C and 1,5-dibromopentane (2.5 ml, 18.4 mmol) was added. The solution was allowed to warm to ambient temperature and stirred for 2 h. The reaction mixture was hydrolysed with water (2 ml) and the solvent removed in a vacuum. The product was extracted with dichloromethane (3 $\times$ 20 ml) and the combined organic extracts washed with water (3 $\times$ 20 ml), followed by bulb-to-bulb distillation (145°C, 0.2 Torr) to give a pale yellow oil (1.28 g, 30% but variable 5–30%). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 6.87 (d, $^3J = 1.28$ Hz, 2, *H*4 or *H*5), 6.75 (d, $^3J =$ 1.26 Hz, 2, *H*4 or *H*5), 3.52 (s, 6, N–CH_3), 4.06 (t, $^3J = 5.14$ Hz, 4, mimCH_2), 1.78 (q, $^3J = 7.68$ Hz, 4, mimCH_2CH_2), 1.50 (m, 2, mim$CH_2CH_2CH_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 50 MHz): δ 148.9 (*C*1), 127.4 (*C*4), 120.8 (*C*3), 33.0 (N–CH_3), 29.6 (mimCH_2CH_2), 27.9 (mimCH_2CH_2), 27.1 (mim$CH_2CH_2CH_2$). Anal. Calc. for $C_{13}H_{20}N_4$: C, 67.21; H, 8.68; N, 24.12. Found: C, 67.20; H, 8.86; N, 24.21%.

*4.1.4. 1,3-Bis(pyrazol-1-ylmethyl)benzene (**4**)*

This previously reported compound [5] was made by a modified procedure. Pyrazole (1.13 g, 16.6 mmol) was

added to a stirred suspension of finely cut potassium (0.62 g, 15.9 mmol) in tetrahydrofuran (40 ml) under an argon atmosphere. The mixture was heated to reflux and maintained at this temperature until beads of molten potassium were no longer evident (~ 1 h). The resultant white suspension was cooled to ambient temperature and 1,3-bis(bromomethyl)benzene (2.00 g, 7.6 mmol) added in one portion. The reaction mixture was refluxed overnight, then quenched by addition of water (0.1 ml), filtered and the solvent removed in a vacuum. The product was purified by bulb-to-bulb distillation to give a clear oil that formed as a white solid (165°C, 0.2 Torr), (1.59 g, 88%). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.55 (d, $^3J = 1.8$ Hz, 2, *H*3-pz), 7.38 (d, $^3J = 2.3$ Hz, 2, *H*5-pz), 7.29 (t, $^3J = 7.7$ Hz, 2, *H*5), 7.12 (d, $^3J = 7.8$ Hz, 2, *H*4, *H*6), 7.06 (s, 1, *H*2), 6.28 ('t', 2, *H*4-pz), 5.31 (s, 4, $C_6H_4(CH_2)_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 50 MHz): δ 139.6, 137.3, 129.3, 129.3, 127.1, 126.6, 106.0, 55.5.

4.2. Synthesis of complexes

4.2.1. Pd{CH(CH$_2$CH$_2$py)$_2$-N,C,N′}Cl (**5**)

A solution of palladium(II) acetate (0.20 g, 0.89 mmol) and 1,5-bis(pyridin-2-yl)pentane (0.24 g, 1.05 mmol) in glacial acetic acid (3 ml) was stirred at 110°C for 3 h. The solvent was removed in a vacuum at 50°C to give a yellow oil. The oil was dissolved in acetone (5 ml), lithium chloride (0.4 g) was added and the solution stirred for 15 h. The solvent was removed in a vacuum, the residue was extracted with dichloromethane (20 ml), and the solution filtered through Celite and the solvent removed in a vacuum. The resulting yellow oil was dissolved in dichloromethane (1 ml) and impurities precipitated by addition of petroleum ether (5 ml, b.p. 60–80°C). The solution was decanted and the solvent removed in a vacuum. The resulting yellow oil was dissolved in acetonitrile (0.4 ml), from which the product precipitated as a yellow powder (0.04 g, 12%). Crystals suitable for single-crystal X-ray structure determination were grown from a $CHCl_3$–petroleum ether (b.p. 60–80°C) solution. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 9.41 (dd, $^3J = 5.7$ Hz, $^5J = 1.8$ Hz, 2, *H*6), 7.68 (m, 2, *H*4), 7.26 (m, 2, *H*3), 7.15 (m, 2, *H*5), 3.45–3.30 (m, 2, pyCH_2), 3.02–2.90 (m, 2, pyCH_2), 2.56 (m, 1, pyCH$_2$CH$_2$C*H*), 1.35–1.05 (m, 4, pyCH$_2$CH_2). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): δ 162.1 (*C*6), 155 (*C*2), 138.2 (*C*4), 124.4 (*C*3), 121.7 (*C*5), 40.0 (py*C*H$_2$), 37.0 (pyCH$_2$CH$_2$*C*H), 32.9 (pyCH$_2$*C*H$_2$). Anal. Calc. for $C_{15}H_{17}N_2Pd$: C, 49.07; H, 4.67; N, 7.63. Found: C, 48.96; H, 4.72; N, 7.72%.

4.2.2. Pd{CH(CH$_2$CH$_2$pz)$_2$-N,C,N′}Cl (**6**)

A solution of palladium(II) acetate (0.10 g, 0.45 mmol) and 1,5-bis(pyrazol-1-yl)pentane (0.10 g, 0.49 mmol) in acetic acid (5 ml) was stirred at 100°C for 20 h. The solvent was removed in a vacuum at 50°C leaving a yellow oil. The oil was dissolved in acetone (5 ml) and lithium chloride (0.1 g) was added to the solution, which was stirred overnight. The solvent was stripped on a rotary evaporator and the product extracted with dichloromethane (3 × 2 ml). The solution was filtered through Celite and the solvent removed in a vacuum. The resultant yellow oil was dissolved in acetone (1 ml) and cooled to − 20°C for 4 h. After this time the product had crystallised, the solution was decanted and the product washed with petroleum ether (b.p. 60–80°C) (3 × 2 ml). The product was recrystallised from CH_2Cl_2–petroleum ether (b.p. 60–80°C) and finally dried in a vacuum to give a pale yellow solid (0.054 g, 35%). Crystals suitable for single crystal X-ray structure determination were grown from a CH_2Cl_2–petroleum ether (b.p. 60–80°C) solution. ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 8.41 (d, $^3J = 2.36$ Hz, 2, *H*3), 7.42 (d, $^3J = 2.57$ Hz, 2, *H*5), 6.26 ('t', 2, *H*4), 4.53–4.40 (m, 2, pzCH_2), 4.22–4.10 (m, 2, pzCH_2), 2.54 (m, 1, pzCH$_2$CH$_2$C*H*), 1.73–1.56 (m, 2, pzCH$_2$CH_2), 1.49–1.31 (m, 2, pzCH$_2$CH_2). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 144.9 (*C*3), 131.6 (*C*5), 106.6 (*C*4), 52.0 (pz*C*H$_2$), 34.4 (pzCH$_2$*C*H$_2$), 28.4 (pzCH$_2$CH$_2$*C*H). Anal. Calc. for $C_{11}H_{15}ClN_4Pd$: C, 38.28; H, 4.38; N, 16.23. Found: C, 38.58; H, 4.34; N, 16.01%.

4.2.3. Pd{CH(CH$_2$CH$_2$mim)$_2$-N,C,N′}Cl (**7**)

A solution of palladium(II) acetate (0.79 g, 3.5 mmol) and 1,5-bis(*N*-methylimidazol-2-yl)pentane (0.91 g, 3.9 mmol) in acetic acid (40 ml) was stirred at 110°C for 5 h. The solvent was removed in a vacuum at 50°C leaving a brown oil. The oil was dissolved in acetone (100 ml) and lithium chloride (1 g) in water (10 ml) was added to the solution, which was stirred overnight. The solvent was stripped on a rotary evaporator and the product extracted with dichloromethane (3 × 50 ml). The combined organic extracts were washed with water (3 × 100 ml) and then dried over $MgSO_4$. The solution was filtered and the solvent removed in a vacuum to give a tan solid (0.22 g, 17%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.02 (d, $^3J = 1.66$ Hz, 2, *H*4), 6.70 (d, $^3J =$ 1.64 Hz, 2, *H*5), 3.55 (s, 6, N–CH_3), 2.93–2.82 (m, 2, mimCH_2), 2.68–2.60 (m, 2, mimCH_2), 2.25 (m, 1, mimCH$_2$CH$_2$C*H*), 1.87–1.70 (m, 2 mimCH$_2$CH_2), 1.15–1.05 (m, 2, mimCH$_2$CH_2. ^{13}C{^{1}H}-NMR ($CDCl_3$, 50 MHz): δ 148.76 (*C*2), 130.97 (*C*4), 119.65 (*C*5), 33.47 (N–*C*H$_3$), 32.95 (mim*C*H$_2$), 32.78 (mimCH$_2$CH$_2$-*C*H), 25.55 (mimCH$_2$*C*H$_2$).

4.2.4. [Pd{CH(CH$_2$CH$_2$pz)$_2$-N,C,N′}(OCMe$_2$)][BF$_4$] (**8**)

To a suspension of **6** (0.050 g, 0.15 mmol) in acetone (1 ml) was added a solution of $AgBF_4$ (0.028 g, 0.15 mmol) in acetone (1 ml) and the mixture was stirred overnight. The solution was filtered through Celite and the solvent reduced to a minimum in a vacuum. Yellow

crystals formed on standing which were collected by decanting the remaining solution, and then dried in a vacuum to give yellow crystals (0.023 g, 34%). Crystals suitable for single-crystal X-ray structure determination were grown from an acetone solution. ^{1}H-NMR (acetone-d_6, 200 MHz): δ 8.01 (d, $^3J = 2.43$ Hz, 2, *H*5), 7.52 (d, $^3J = 2.14$ Hz, 2, *H*3), 6.46 ('t', 2, *H*4), 4.79–4.66 (m, 2, pzCH_2), 4.44–4.31 (m, 2, pzCH_2), 2.97 (m, 1, pzCH$_2$CH$_2$C*H*), 1.85–1.65 (m, 2, pzCH$_2$CH_2), 1.35–1.19 (m, 2, pzCH$_2$CH_2). ^{13}C{^{1}H}-NMR (acetone-d_6, 50 MHz): δ 42.5 (*C*3), 134.6 (*C*5), 108.1 (*C*4), 52.5 (pz*C*H$_2$), 34.8 (pzCH$_2$*C*H$_2$), 32.6 (pzCH$_2$CH$_2$*C*H). Anal. Calc. for $C_{14}H_{21}BF_4N_4OPd$: C, 36.99; H, 4.66; N, 12.33. Found: C, 36.79; H, 4.60; N, 12.49%.

4.2.5. PdCl{2,6-(pzCH$_2$)$_2$C$_6$H$_3$} (9)

A solution of $PdCl_2$(1,5-cyclooctadiene) (0.10 g, 0.35 mmol) and 1,3-bis(pyrazol-1-ylmethyl)benzene (**4**) (0.084 g, 0.35 mmol) in acetonitrile (15 ml) was stirred overnight. The solution was decanted and the insoluble product was washed with acetonitrile (5 ml), acetone (5 ml) and petroleum ether (40–60°) (5 ml). The resultant orange–yellow product, $PdCl_2\{1,3\text{-}(pzCH_2)_2C_6H_3\}$, was dried in a vacuum (0.113 g, 77%). This complex was insoluble in standard NMR solvents. Anal. Calc. for $C_{14}H_{14}Cl_2N_4Pd$, C: 40.46; H: 3.40; N: 13.48. Found, C: 40.41; H: 3.42; N: 13.61%. The complex (0.125 g, 0.30 mmol) was placed in a flask on a bulb-to-bulb distillation apparatus. The flask was evacuated and heated with rotation to 230°C and maintained at this temperature until the solid changed colour from orange/yellow to grey. The product was extracted with CH_2Cl_2 (50 ml) and filtered through Celite. The solvent was reduced in a vacuum to $\sim$2 ml and the product precipitated by the addition of diethyl ether (20 ml). The product was collected by filtration and dried in a vacuum leaving a white powder (0.060 g, 53%). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 8.17 (d, $^3J = 2.2$ Hz, 2, *H*3-pz), 7.61 (d, $^3J = 2.8$ Hz, 2, *H*5-pz), 7.06 (s, 3, C$_6H_3$(CH$_2$)$_2$), 6.33 ('t', 2, *H*4-pz), 5.34 (sb, 4, C$_6$H$_3$(CH_2)$_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 50 MHz): δ 144.5, 136.4, 131.5, 126.7, 125.3, 107.1, 58.9. Anal. Calc. for $C_{14}H_{13}ClN_4Pd$: C, 44.35; H, 3.46; N, 14.78. Found: C, 44.30; H, 3.33; N, 14.27%.

4.2.6. [Pd(OH$_2$){2,6-(pzCH$_2$)$_2$C$_6$H$_3$}][BF$_4$] (10)

A solution of $AgBF_4$ (0.055 g, 0.29 mmol) in water (3.0 ml) was added to a stirred suspension of PdCl{2,6-(pzCH$_2$)$_2$C$_6$H$_3$} (**9**) (0.108 g, 0.29 mmol) in acetone (40 ml). The solution was stirred in the absence of light for 10 min. The solution was filtered and the solvent removed in a vacuum. The residue was extracted with acetone (3 ml) and the product crystallised as yellow crystals on addition of diethyl ether (0.087 g, 67%). Crystals suitable for single-crystal X-ray structure determination were grown from a solution of acetone–diethyl ether. ^{1}H-NMR (acetone-d_6, 200 MHz): δ 8.20 (d, $^3J = 2.5$ Hz, 2, *H*3-pz), 7.79 (d, $^3J = 1.8$ Hz, 2, *H*5-pz), 7.19–7.03 (m, 3, C$_6H_3$(CH$_2$)$_2$), 6.49 ('t', 2, *H*4-pz), 5.61 (s, 4, C$_6$H$_3$(CH_2)$_2$). ^{13}C{^{1}H}-NMR (acetone-d_6, 50 MHz): δ 143.1, 137.5, 134.4, 128.0, 126.8, 108.3, 58.6. Anal. Calc. for $C_{14}H_{15}BF_4N_4PdO$: C, 37.49; H, 3.37; N, 12.49. Found: C, 37.71; H, 3.37; N, 12.39%.

4.2.7. Thermogravimetric analysis

The complex $PdCl_2\{1,5\text{-}(pzCH_2)_2C_6H_4\}$ (0.01209 g, 0.029 mmol) was placed in an aluminium oxide TGA crucible, and under an argon gas flow the sample was heated from 150–300°C at a rate of 2° min^{-1} (Setaram TGA 92). The sample lost 0.01210 g in the range 180–280°C, a loss of 10.0% (Calc. for loss of HCl 8.8%). On cooling the sample was dissolved in $CDCl_3$ to give a ^{1}H-NMR spectrum identical to that of PdCl{2,6-(pzCH$_2$)$_2$C$_6$H$_3$} (**9**).

4.3. X-ray data collection, structure determination and refinement for complexes 5, 6, 8 and 10

Room temperature single counter/four-circle diffractometer data sets were measured to the specified redundancy within the specified $2\theta_{max}$ limit ($2\theta/\theta$ scan mode; monochromatic Mo–K$_\alpha$ radiation, $\lambda = 0.7107_3$ Å; *T* ca. 295 K) yielding N_t total reflections, these being merged to N_r unique (R_{int} quoted), N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinements, Gaussian absorption corrections being applied. Anisotropic thermal parameters were refined for the non-hydrogen atoms (*x*, *y*, *z*, $U_{iso})_H$ being included constrained at estimated values. Conventional residuals *R*, R_w on $|F|$ are quoted at convergence, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being applied. Neutral atom complex scattering factors were employed, computation using the XTAL 3.4 program system [18].

For complex **5** N_t (sphere) = 13 086, $R_{int} = 0.11$.

For complex **6**, conformational disorder, most pronounced in the aliphatic component of segment 1 of the ligand was modelled in terms of individual pairs of atom components for C(0, 121), with site occupancies set at 0.5 after trial refinement. Unique data.

The crystal of complex **8** (capillary mounted) decomposed by ca. 70% during data collection, appropriate scaling being applied. The anion was modelled as disordered over two sets of sites, occupancies set at $x = 0.85(2)$, $1 - x$ after preliminary refinement. The coordinated ligand was modelled as acetone on the basis of geometry and refinement behaviour. Large displacement amplitudes in the hydrocarbon string are presumed to indicate unresolved disorder. N_t (hemisphere) = 6476, $R_{int} = 0.045$.

In **10**, similar anion disorder was resolved and refined, *x* being 0.73(1), for *F*(2–4), rotationally disor-

dered about B–F(1). N_t (hemisphere) = 7844, R_{int} = 0.017.

5. Supplementary material

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre (deposition nos.: 147416–147419). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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