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Synthesis of methylpalladium(II) cationic complexes from $[PdMe(SMe_2)(\mu\text{-}I)]_2$. Crystal structure of $[PdMe(bpy)(\gamma\text{-pic})]BF_4$

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Abstract

The complex $[PdMe(SMe_2)(\mu\text{-}I)]_2$ is a suitable reagent for the synthesis of methylpalladium(II) cationic complexes. Addition of 2,2′:6′,2″-terpyridyl or 2,2′-bipyridyl to $[PdMe(SMe_2)(\mu\text{-}I)]_2$ gives [PdMe(terpy)]I or PdIMe(bpy), respectively, and the latter complex reacts with $AgBF_4$ in acetonitrile to give $[PdMe(bpy)(NCMe)]BF_4$. Addition of bpy and $AgBF_4$ to $[PdMe(SMe_2)(\mu\text{-}I)]_2$ in acetone, followed by filtration and addition of γ-picoline or acetonitrile to the filtrate, gives $[PdMe(bpy)(\gamma\text{-pic})]BF_4$ or $[PdMe(bpy)(SMe_2)]BF_4$, respectively. The crystal structure of $[PdMe(bpy)(\gamma\text{-pic})]BF_4$ has been determined and shows that the cation $[PdMe(bpy)(\gamma\text{-pic})]^+$ has square planar coordination at palladium(II) and the γ-picoline plane forms an angle of 62.1° with the '$PdCN_3$' coordination plane.

Introduction

As part of an investigation of the organometallic chemistry of palladium(IV) we have recently developed synthetic routes to methylpalladium(II) and dimethylpalladium(II) complexes of aromatic nitrogen donor ligands, e.g. the 2,2′-bipyridyl complexes PdXMe(bpy)(X = Cl, Br, I) and $PdMe_2$(bpy) [1–3]. The complex $[PdMe(SMe_2)(\mu\text{-}I)]_2$ [1,4] was found to be an excellent precursor for the synthesis of a range of methylpalladium(II) complexes during this work, and in a related report $[PdMe(SMe_2)(\mu\text{-}Cl)]_2$ [4] has been used for the synthesis of PdClMe(2,9-Me_2phen) [5]. We have found the iodo dimer to be particularly useful, as it may be isolated in a higher yield (85–91%) than the chloro (45%) and bromo (70%) analogues, and its synthesis does not require 'halide-free' MeLi. It may also be used to prepare chloro

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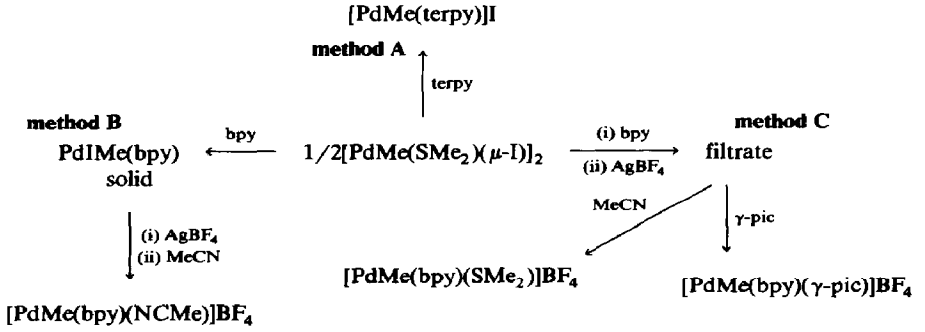
and bromo complexes by halide exchange, e.g. addition of $AgNO_3$ to $[PdMe(SMe_2)(\mu\text{-}I)]_2$ in acetonitrile followed by filtration and addition of KBr and PPh_3 gives *trans*-$PdBrMe(PPh_3)_2$ in 82% yield [2,3]. Syntheses involving removal of the bridging iodo ligand from $[PdMe(SMe_2)(\mu\text{-}I)]_2$ indicate that this reagent may be useful for the synthesis of cationic complexes, which for alkylpalladium(II) nitrogen donor chemistry appear to be limited to a few intramolecular coordination systems, e.g. $[Pd(CHMeCHMeNMe_2)(NHMe_2)_2]CF_3SO_3$ [6]. We report here a general route to methylpalladium(II) cationic complexes, and the crystal structure of the γ-picoline complex $[PdMe(bpy)(\gamma\text{-pic})]BF_4$. A preliminary account of part of this work has been published [2], and in a more recent report [7] the tetramethylethylenediamine complex $[PdMe(tmeda)(NCMe)]CF_3SO_3$ has been obtained by an oxidative addition–reductive elimination sequence involving reaction of methyl triflate with $PdMe_2(tmeda)$.

Results and discussion

Synthesis and characterisation of complexes

Three synthetic routes to cationic complexes from $[PdMe(SMe_2)(\mu\text{-}I)]_2$ have been developed (Scheme 1). Addition of the planar tridentate ligand 2,2′ : 6′,2″-terpyridyl gave [PdMe(terpy)]I directly (method A), but, as expected for the bidentate ligand 2,2′-bipyridyl, alternative procedures are required as this ligand gives the neutral complex PdIMe(bpy) with retention of the coordinated iodo ligand [3]. Addition of $AgBF_4$ and acetonitrile to a suspension of PdIMe(bpy) in acetone gave $[PdMe(bpy)(NCMe)]BF_4$ (method B). However, if $AgBF_4$ is added to the suspension of PdIMe(bpy) obtained directly from $[PdMe(SMe_2)(\mu\text{-}I)]_2$ and bpy in acetone, and the resulting AgI collected, the filtrate gives $[PdMe(bpy)(SMe_2)]BF_4$ on addition of acetonitrile (method C). Thus, dimethylsulfide is preferred as a ligand to acetonitrile, but the stronger donor γ-picoline readily gives $[PdMe(bpy)(\gamma\text{-pic})]BF_4$. The complexes are stable at ambient temperature and give satisfactory microanalyses, in contrast to $[PdMe(tmeda)(NCMe)]CF_3SO_3$ which is unstable [7].

The complexes give satisfactory ^1H NMR spectra in $CDCl_3$ and $(CD_3)_2CO$, except for [PdMe(terpy)]I which required $CD_3OD/(CD_3)_2SO$ for dissolution. The complexes $[PdMe(bpy)(L)]BF_4$ (L = SMe_2, MeCN, γ-pic) in $CDCl_3$ exhibited resonances for two inequivalent pyridyl rings for the bpy ligand, as shown in Fig. 1 for the γ-pic complex. However, in $(CD_3)_2CO$ the complexes with L = SMe_2 or CH_3CN show broad resonances at ambient temperature indicative of exchange between L



Scheme 1. Synthesis of methylpalladium(II) cationic complexes in acetone at ambient temperature.

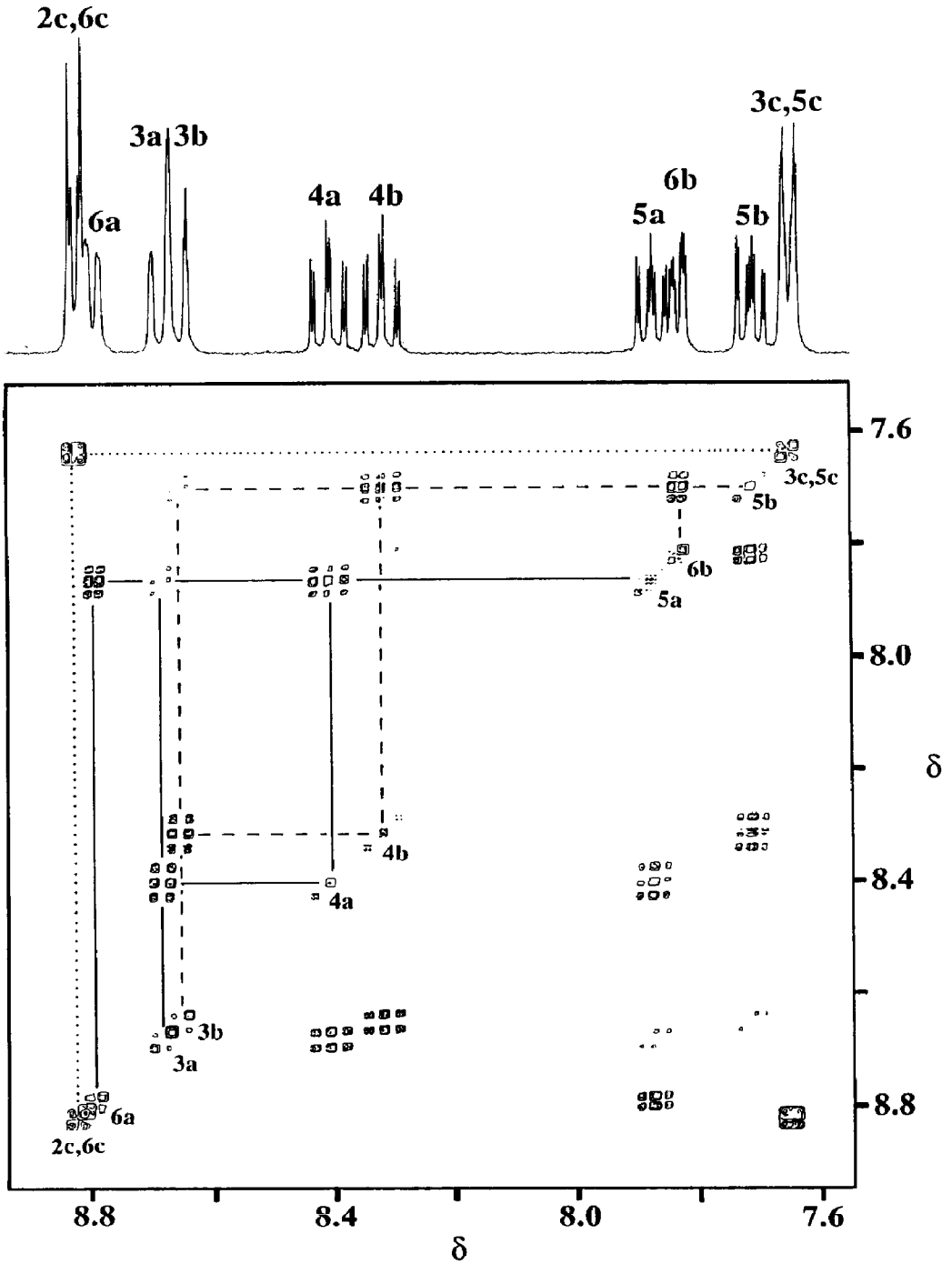


Fig. 1. ^{1}H NMR spectrum and COSY diagram for the aromatic region of [PdMe(bpy)(γ-pic)]BF_4 when dissolved in $(CD_3)_2CO$, illustrating the determination of connectivity within ring systems and the marked upfield shift for the proton 6b of the pyridyl ring adjacent to the γ-picoline ligand compared with the analogous proton 6a adjacent to the PdMe group. The labelling of hydrogen atoms is identical to that for the carbon atoms in Fig. 2. Ring 'a': ———; ring 'b': - - - - - -; ring 'c' (γ-pic): · · · · · · ·

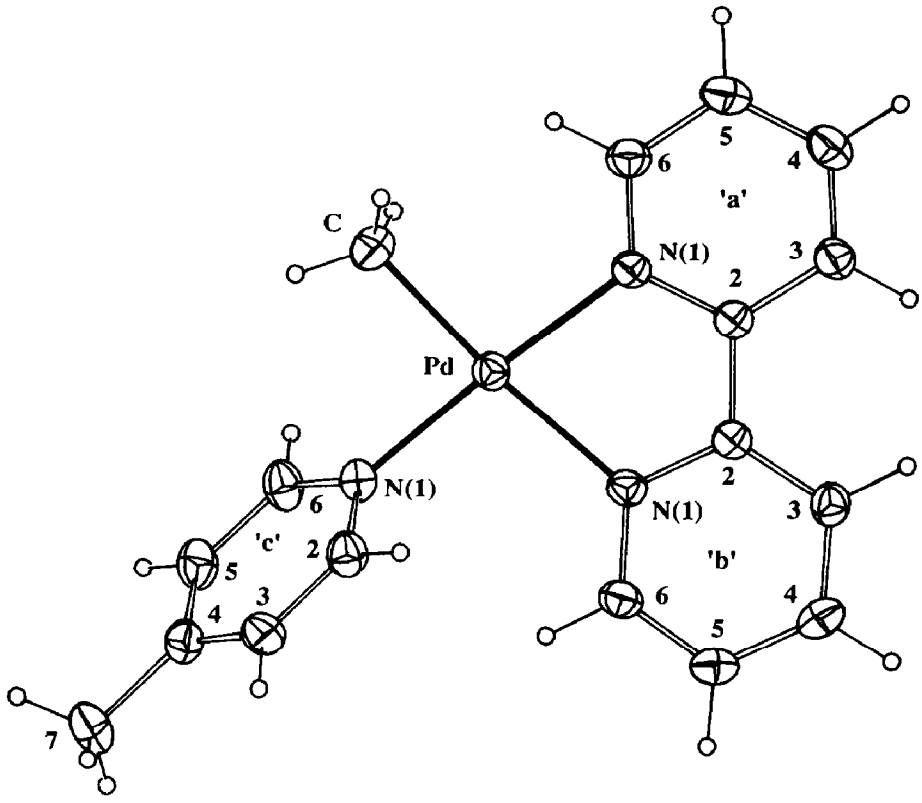


Fig. 2. The cation $[PdMe(bpy)(\gamma\text{-pic})]^+$ projected normal to the '$PdCN_3$' coordination plane; 20% thermal ellipsoids are shown for the non-hydrogen atoms, and hydrogen atoms (constrained at estimated idealized positions) have been given an arbitrary radius of 0.1 Å.

and $(CD_3)_2CO$, resulting in exchange of pyridyl environments trans to PdMe and PdL. Resonances for the pyridyl rings were resolved for the γ-pic complex in $(CD_3)_2CO$ or CD_3CN, but in C_5D_5N similar behaviour to that for the other complexes was observed, again indicative of exchange between γ-pic and the stronger donor solvent C_5D_5N.

Spectra were fully assigned with the aid of spin correlation spectroscopy (COSY) spectra, e.g. as illustrated in Fig. 1. Ring b is assigned to the set of pyridyl resonances having H(6) 0.97 ppm upfield from that of ring a. An upfield shift is expected to arise from anisotropic shielding by the γ-pic ring, which is sterically prevented from lying coplanar with the coordination plane and forms an angle of 62.1° with this plane in the solid state (Fig. 2). Assignment of the pyridyl rings in the bpy ligand for $[PdMe(bpy)(L)]BF_4$ (L = NCMe, SMe_2) was not attempted, although protons within each ring system are assigned.

Crystal structure of $[PdMe(bpy)(\gamma\text{-pic})]BF_4$

Selected bond distances and angles are given in Table 1, and a projection normal to the coordination plane is given in Fig. 2. The anion is well removed from the cation, with Pd · · · F(3) 3.981(5) Å. The pyridyl rings are planar, and the rings of 2,2′-bipyridyl form dihedral angles of 2.1° to the 'CN_3' coordination plane and 1.5°

Table 1

Coordination geometry for the palladium atom in [PdMe(bpy)(γ-pic)]BF_4 (distances in Å, angles in degrees)

Pd–C [a]	2.036(6)	Pd–N(b1)	2.131(4)
Pd–N(a1)	2.049(4)	Pd–N(c1)	2.033(4)
C–Pd–N(a1)	95.4(2)	Pd–N(a1)–C(a2)	116.0(3)
C–Pd–N(b1)	174.3(2)	Pd–N(a1)–C(a6)	125.8(3)
C–Pd–N(c1)	88.1(2)	Pd–N(b1)–C(b2)	113.1(3)
N(a1)–Pd–N(b1)	79.1(2)	Pd–N(b1)–C(b6)	128.8(3)
N(a1)–Pd–N(c1)	176.4(2)	Pd–N(c1)–C(c2)	120.9(4)
N(b1)–Pd–N(c1)	97.4(2)	Pd–N(c1)–C(c6)	121.0(3)
Deviation (Å) of atoms from the 'CN$_3$' plane [b]			
Pd	0.002	N(b1)	−0.016
C	−0.037	N(c1)	0.017
N(a1)	0.017		

[a] The shortest Pd···F contact is Pd···F(3), 3.981(5) Å. [b] The mean plane has χ^2 51.6. The 'C$_5$N' rings (a, b, c) have χ^2 1.2, 7.4, and 2.4, respectively; they form dihedral angles of 2.1, 2.1, and 62.1° with the 'C$_3$N' plane, the Pd atom lies 0.061, 0.001 and 0.117 Å from the mean planes, and the two planes of bpy form a dihedral angle of 1.5°.

to each other. The coordination mean plane has the atoms C(1), Na(a1, b1, c1) alternately above and below the plane by ca. 0.016 Å, except for N(c1) at −0.037 Å, and the Pd atom lies 0.002 Å from the plane. Palladium(II)-methyl distances have been determined for several complexes [4,7,8]; the most closely related complex, containing only methyl groups and nitrogen donor atoms bonded to palladium is $PdMe_2$(tmeda). This complex has Pd–C 2.026(3) and 2.029(3) Å, essentially identical to the present complex, 2.036(6) Å. The *trans* influence of the methyl group in [PdMe(bpy)(γ-pic)]$^+$ is apparent, since Pd–N(b1) [2,131(4) Å] is much longer than the Pd–N bonds *trans* to each other [2.049(4) and 2.033(4) Å], although Pd–N(b1) is significantly shorter than in $PdMe_2$(tmeda) [2.197(2) and 2.200(2) Å].

Concluding remarks

The synthesis of methylpalladium(II) cationic complexes is readily achieved from [PdMe(SMe_2)(μ-I)]$_2$ and PdIMe(L_2) (L_2 = bidentate nitrogen donor), explored here for representative tridentate and bidentate ligands. Of particular interest is the facile synthesis of [PdMe(bpy)(L)]$^+$ (L = MeCN, SMe_2), since the replacement of L by more strongly coordinating ligands, e.g. SMe_2 for MeCN and γ-pic for SMe_2, indicates that complexes of this type are ideal reagents for the development of a wider range of complexes. For acetonitrile as a ligand, the isolation of PdIMe(L_2) is required, but complexes of this type are readily obtained from [PdMe(SMe_2)(μ-I)]$_2$ [1–3]. Alternative routes to PdIMe(L_2) are available, e.g. reaction of *trans*-$PdCl_2(SMe_2)_2$ with MgMeI or MeLi (prepared from metal and MeI) and subsequent addition of L_2 [1,3], reaction of MeI with $PdMe_2(L_2)$ [7,9,10], or reductive elimination of ethane from $PdIMe_3(L_2)$ in the solid state [9]. However, the latter two routes, involving the intermediacy of palladium(IV) complexes, require more careful control of reaction conditions, and require halide free MeLi for the synthesis of $PdMe_2(L_2)$ [7,9–11].

Experimental

The reagents $[PdMe(SMe_2)(\mu\text{-}I)]_2$ [4] and PdIMe(bpy) [3] were prepared as previously described. Microanalyses were performed by the Canadian Microanalytical Service, Vancouver. ^1H NMR spectra were recorded with a Bruker AM 300 spectrometer, and chemical shifts are given in ppm relative to Me_4Si. For the 2,2′-bipyridyl complexes, chemical shift data are given for solutions of the complexes in solvents that give the maximum separation of resonances for pyridyl rings trans to PdMe and Pd(L) (L = γ-pic, SMe_2, MeCN).

Synthesis of complexes

[PdMe(bpy)(γ-pic)]BF_4. 2,2′-Bipyridyl (0.15 g, 0.96 mmol) was added to a stirred suspension of $[PdMe(SMe_2)(\mu\text{-}I)]_2$ (0.30 g, 0.48 mmol) in acetone (40 ml). A solution of $AgBF_4$ (0.19 g, 0.97 mmol) in acetone (10 ml) was added, followed by γ-picoline (ca. 0.2 ml). The precipitated AgI was filtered off, and hexane was added to the filtrate. Partial removal of acetone by rotary evaporation at 0 °C gave yellow crystals of the complex. The product was recrystallised from acetone/hexane (0.28 g, 65%). Anal. Found: C, 44.5; H, 4.0; N, 9.1, $C_{17}H_{18}BF_4N_3Pd$ calcd.: C, 44.6; H, 4.0; N, 9.2%. ^1H NMR ($(CD_3)_2CO$) (Fig. 1); δ, py trans to PdMe: 8.67 (1H, m, H(3)), 8.33 (1H, m, H(4)), 7.84 (1H, m, H(6)), 7.72 (1H, m, H(5)); py trans to γ-pic: 8.81 (1H, db, H(6)), 8.70 (1H, m, H(3)), 8.42 (1H, m, H(4)), 7.88 (1H, m, H(5)); γ-pic: 8.84 (2H, m, H(2, 6)), 7.66 (2H, m, H(3, 5)), 2.56 (3H, s, Me); 0.90 (3H, s, PdMe).

[PdMe(bpy)(SMe_2)]BF_4. The above procedure, with acetonitrile in place of γ-picoline, gave $[PdMe(bpy)(SMe_2)]BF_4$ as fine white needles (63%). Anal. Found: C, 36.6; H, 4.0; N, 6.6, $C_{13}H_{17}BF_4N_2PdS$ calcd.: C, 36.6; H, 4.0; N, 6.6%. ^1H NMR ($CDCl_3$); δ, py ring I: 8.74 (1H, d, H(6)), 8.51 (1H, d, H(3)), 8.21 (1H, m, H(4)), 7.73 (m, H(5)); py ring II: 8.61 (1H, d, H(6)), 8.56 (1H, d, H(3)), 8.27 (1H, m, H(4)), 7.71 (m, H(5)); 2.55 (6H, s, SMe_2); 1.01 (3H, s, PdMe).

[PdMe(bpy)(NCMe)]BF_4. The above procedure, with PdIMe(bpy) in place of $[PdMe(bpy)(\mu\text{-}I)]_2$, gave $[PdMe(bpy)(NCMe)]BF_4$. Recrystallisation was unnecessary (76%). Anal. Found: C, 38.2; H, 3.5; N, 10.2, $C_{13}H_{14}BF_4N_3Pd$ calcd.: C, 38.5; H, 3.5; N, 10.4%. ^1H NMR (CD_3CN) at 0 °C; δ, py ring I: 8.54 (1H, d, H(6)), 8.29 (m, H(3)), 8.20 (m, H(4)), 7.70 (m, H(5)); py ring II: 8.49 (1H, d, H(6)), 8.31 (m, H(3)), 8.23 (m, H(4)), 7.70 (m, H(5)); 2.02 (3H, s, MeCN); 0.94 (3H, s, PdMe).

[PdMe(terpy)]I. 2,2′:6′,2″-Terpyridyl (0.15 g, 0.64 mmol) was added to a solution of $[PdMe(SMe_2)(\mu\text{-}I)]_2$ (0.2 g, 0.32 mmol) in acetone (40 ml). The complex separated out immediately (87%), and recrystallisation was unnecessary. Anal. Found: C, 39.5; H, 2.9; N, 8.6, $C_{16}H_{14}BF_4N_3Pd$ calcd.: C, 39.9; H, 2.9; N, 8.7%. ^1H NMR ($CD_3OD/(CD_3)_2SO$): δ 8.10 (2H, m, H(6, 6″)), 7.97 (2H, m, H(3, 3″)), 7.94–7.84 (3H, m, H(3′, 4′, 5′)), 7.81 (2H, m, H(4, 4″)), 7.28 (2H, m, H(5, 5″)), 1.09 (3H, s, PdMe).

X-Ray structural determination

A unique data set for $[PdMe(bpy)(\gamma\text{-pic})]BF_4$ was measured at ca. 295 K to $2\theta_{max} = 50°$ using a Syntex $P2_1$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode. 3216 independent reflections were measured, 2368 with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least squares refinement after

Table 2

Non-hydrogen atom coordinates for [PdMe(bpy(γ-pic)]BF_4.

Atom	x	y	z
Pd	0.19928(5)	0.04912(3)	0.13336(2)
C	0.3029(7)	0.1949(5)	0.1281(3)
2,2′-bipyridyl			
N(a1)	0.2364(5)	0.0061(3)	0.0239(2)
C(a2)	0.1826(6)	−0.0910(4)	0.0015(3)
C(a3)	0.2056(7)	−0.1304(4)	−0.0705(3)
C(a4)	0.2824(7)	−0.0696(5)	−0.1195(3)
C(a5)	0.3359(7)	0.0292(5)	−0.0978(3)
C(a6)	0.3123(7)	0.0653(4)	−0.0262(3)
N(b1)	0.0896(5)	−0.1038(3)	0.1268(2)
C(b2)	0.0996(6)	−0.1521(4)	0.0582(3)
C(b3)	0.0342(7)	−0.2523(4)	0.0434(3)
C(b4)	−0.0419(7)	−0.3031(4)	0.0996(3)
C(b5)	−0.0541(7)	−0.2539(4)	0.1686(3)
C(b6)	0.0114(6)	−0.1547(4)	0.1795(3)
γ-picoline			
N(c1)	0.1589(5)	0.0821(3)	0.2433(2)
C(c2)	0.2232(7)	0.0214(4)	0.3013(3)
C(c3)	0.1903(7)	0.0379(5)	0.3755(3)
C(c4)	0.0889(7)	0.1199(4)	0.3938(3)
C(c5)	0.0263(7)	0.1817(5)	0.3330(3)
C(c6)	0.0621(7)	0.1623(5)	0.2595(3)
C(c7)	0.0472(9)	0.1400(6)	0.4739(4)
anion			
B	0.8287(9)	0.4109(5)	0.1719(4)
F(1)	0.9225(6)	0.3949(4)	0.1169(2)
F(2)	0.7286(6)	0.3302(4)	0.1802(3)
F(3)	0.9306(6)	0.4204(5)	0.2355(3)
F(4)	0.7553(8)	0.4989(5)	0.1665(5)

Gaussian absorption correction. Anisotropic thermal parameters were refined for non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were constrained at estimated values. Conventional R, R' on convergence were 0.039, 0.041 (statistical weights, derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0002\ \sigma^4(I_{diff})$). Neutral atom complex scattering factors were used [12]; computation used the XTAL program system implemented by S.R. Hall on a Perkin–Elmer 3241 computer [13]. Coordinates for the non-hydrogen atoms are given in Table 2.

Crystal data: $C_{17}H_{18}BF_4N_3Pd$, M = 457.6, Monoclinic, space group $P2_1/n(C_{2h}^5$, no. 14), a 8.243(2), b 12.632(4), c 17.550(5) Å, β 95.75(2)°, U 1818.2(8) Å^3, D_c (Z = 4) 1.67 g cm^{-3}, F(000) = 912. Monochromatic Mo-K_α radiation, λ 0.7106$_9$ Å, μ_{Mo} 9.8 cm^{-1}, specimen: 0.40 × 0.33 × 0.20 mm, $A^*_{min,max}$ = 1.20, 1.33.

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