New Dimetallic Palladium and Platinum Complexes Containing the Tetrakis(1-pyrazolyl)borate Ligand − Crystal Structures of $[\{(C_6F_5)_2Pd\}_2(\mu\text{-pz})_2B(\mu\text{-pz})_2]^-$, $[\{(C_6F_5)(tBuNC)Pd\}_2(\mu\text{-pz})_2B(\mu\text{-pz})_2]^+$ and $[(C_6F_5)_2Pd(\mu\text{-pz})_2B(\mu\text{-pz})_2Pd(\eta^3\text{-}C_4H_7)]$

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New dimetallic palladium and platinum complexes containing the tetrakis(pyrazol-1-yl)borate ligand of the type $[\{(C_6F_5)_2M\}_2(\mu\text{-pz})_2B(\mu\text{-pz})_2]^-$ (M = Pd, Pt), $[\{(C_6F_5)(L)Pd\}_2(\mu\text{-pz})_2B(\mu\text{-pz})_2]^+$ (L = CN*t*Bu, NCPh, PR_3, AsR_3) and $[\{(C_6F_5)(Cl)Pd\}_2(\mu\text{-pz})_2B(\mu\text{-pz})_2]^-$ have been prepared using the benzonitrile complexes *cis*-$[(C_6F_5)_2M(NCPh)_2]$ (M = Pd, Pt) or the halide bridged complexes $[\{(C_6F_5)LPd(\mu\text{-}X)\}_2]$ (L = CN*t*Bu, NCPh, PR_3, AsR_3, tht; X = Cl or Br), and $[B(pz)_4]^-$ as starting materials. The monometallic $[(C_6F_5)(tBuNC)Pd(\mu\text{-pz})_2B(pz)_2]$ and the asymmetric dinuclear $[(C_6F_5)_2Pd(\mu\text{-pz})_2B(\mu\text{-pz})_2Pd(\eta^3\text{-}C_4H_7)]$ complexes have also been prepared. The crystal structures of $[\{(C_6F_5)_2Pd\}_2(\mu\text{-pz})_2B(\mu\text{-pz})_2]^-$, $[\{(C_6F_5)(tBuNC)Pd\}_2(\mu\text{-pz})_2B(\mu\text{-pz})_2]^+$ and $[(C_6F_5)_2Pd(\mu\text{-pz})_2B(\mu\text{-pz})_2Pd(\eta^3\text{-}C_4H_7)]$ have been established by X-ray diffraction.

Introduction

Poly(pyrazolyl)borates have become an important class of ligands with unique properties, as indicated by the variety of species they form with most metals and metalloids,[1,2] including those of palladium and platinum.[3] This family of ligands has found great favor in studies of structure and reactivity[1−6] relevant to catalysis[7,8] and inorganic biochemistry.[5,9] From a structural coordination chemistry point of view, these polydentate nitrogen-donor ligands offer unique opportunities to look into the detailed dynamic behavior in solution, particularly by use of NMR spectroscopy.[10] Although an important number of monomeric palladium(II) poly(pyrazol-1-yl)borate complexes that have already been structurally characterized by X-ray crystallography exists ($[Pd(COMe)\{(Me_2pz)_2BH_2\text{-}N,N'\}(PCy_3)]$,[11] $[Pd(CH_2SiMe_3)\{(Me_2pz)_2BH_2\text{-}N,N'\}(PMe_3)]$,[12] $[Pd(\eta^3\text{-}C_3H_5)\{(pz)_3BH\text{-}N,N'\}]$, $[PdPh\{(pz)_3BH\text{-}N,N'\}]$, $[PdR\{(pz)_4B\text{-}N,N'\}(PPh_3)]$ (R = Me, Ph),[13] $[Pd\{2\text{-}(NMe_2CH_2)C_{10}H_6\text{-}C,N\}\{(pz)_3BH\text{-}N,N'\}]$,[14] $[Pd\{2\text{-}CH_2\text{-}C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}\{(pz)_3BH\text{-}N,N'\}]$, $[Pd(C_6H_4C_5H_4N\text{-}C^2,N)\{(pz)_3BH\text{-}N,N'\}]$[15]), surprisingly, to the best of our knowledge (3D Search using the Cambridge Structural Database, October 2001 release) there are no dimeric palladium complexes yet fully characterized by X-ray diffraction.

Here, we describe the synthesis and characterization of some new dimetallic palladium and platinum complexes with the tetrakis(pyrazol-1-yl)borate ligand. The crystal structures of $[\{(C_6F_5)_2Pd\}_2(\mu\text{-pz})_2B(\mu\text{-pz})_2]^-$, $[\{(C_6F_5)(tBuNC)Pd\}_2(\mu\text{-pz})_2B(\mu\text{-pz})_2]^+$ and $[(C_6F_5)_2Pd(\mu\text{-pz})_2B(\mu\text{-pz})_2Pd(\eta^3\text{-}C_4H_7)]$ have been established by X-ray diffraction. The benzonitrile complexes *cis*-$[(C_6F_5)_2M(NCPh)_2]$ (M = Pd, Pt) and the halide-bridged complexes $[\{(C_6F_5)LPd(\mu\text{-}X)\}_2]$ (L = CN*t*Bu, NCPh, PR_3, AsR_3, tht; X = Cl or Br) have been shown to be good precursors for the synthesis of the binuclear compounds reported herein.

Results and Discussion

Homodimetallic Complexes 1 and 2

The ready reaction of *cis*-$[(C_6F_5)_2M(NCPh)_2]$ (M = Pd, Pt) in CH_2Cl_2 with $K[B(pz)_4]$ (pz = pyrazolyl) in a 2:1 molar ratio gives the dimetallic complexes **1** and **2** (Scheme 1). The replacement of PhCN by $[B(pz)_4]^-$ takes place without isomerization, and the reaction products are the *cis* isomers. The complexes are air-stable, both in the solid state and in solution, and they are white. The new complexes have been characterized by partial elemental analyses and spectroscopic (IR and ^1H and ^{19}F NMR)

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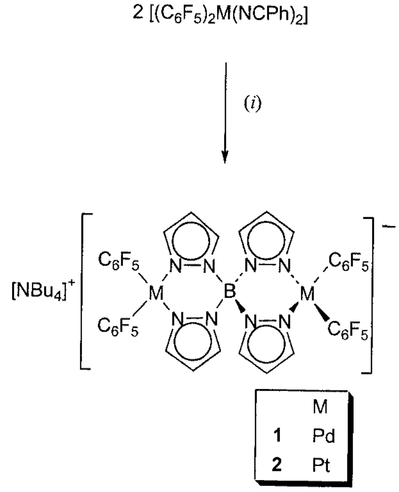
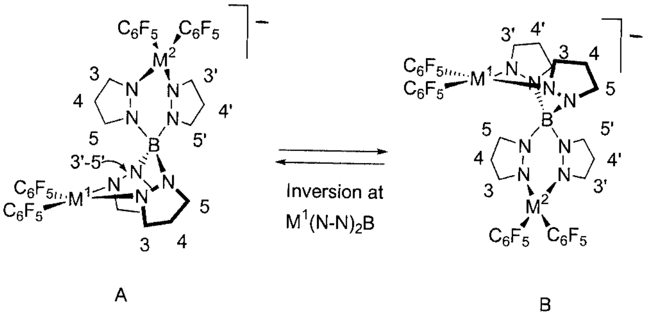
methods. In an acetone solution, these complexes behave as 1:1 electrolytes.[16]



Scheme 1. (*i*) K[B(pz)$_4$]/Bu$_4$NCl

The IR spectra of complexes **1** and **2** show the characteristic absorptions of the C_6F_5 group [17] at 1630, 1490, 1450, 1050, 950 cm^{-1}, and a split band at ca. 800 cm^{-1}, derived from the so-called X-sensitive mode in C_6F_5 halogen molecules, which is characteristic of the *cis*-M(C_6F_5)$_2$ fragment[18,19] and behaves like a ν(M−C) band.[20]

The ^{1}H NMR spectra of **1** and **2** at room temperature show a unique set of three resonances for the pyrazolyl ring protons, which suggests the occurrence of a very fast intramolecular interconversion between the conformational isomers **A** and **B** that arises from the boat like M(N−N)$_2$B ring inversions of these compounds (Scheme 2) for which a spiro structure is expected. The same spectra are observed when the temperature is lowered to −90 °C in CD_2Cl_2. The 3-H and 5-H resonances of complex **1** appear as doublets, owing to coupling with 4-H. The resonance assigned to 4-H appears as a pseudo-triplet. Assignment of the signals to the 3-H and 5-H protons of complex **1** was possible by comparison with the spectrum of complex **2**, for which the 3-H resonance is flanked by satellites (1:4:1) arising from a small hydrogen-platinum coupling. Furthermore, the assignment is also in accordance with the usual criterion for pyrazoles where $^3J_{45} > {}^3J_{34}$.[21]



Scheme 2

We have performed ^{1}H-^{13}C COSY on **1** in order to examine the Onishi criterion[22] for the pyrazolyl C-3 and C-5 NMR assignments in transition-metal poly(1-pyrazolyl)borate complexes, and we have also found that the resonance assigned to the pyrazolyl C-3 CH carbon atoms is at a lower field than that of C-5.

The ^{19}F NMR spectra of **1** and **2** show the presence of four equivalent freely rotating C_6F_5 rings giving three resonances with relative intensities of 2:1:2, due to the *ortho*-, *para*- and *meta*-F atoms, respectively. As expected, the *ortho*-F signal of complex **2** is flanked by satellites due to coupling to ^{195}Pt.

The structure of **1** is shown in Figure 1 and selected bond lengths and angles in Table 1. Insofar as we know, this is the first dipalladium tetrakis(pyrazol-1-yl)borate species to be structurally characterized. The X-ray structure determination of **1** shows the existence of the spiro structure. Both six-membered chelate Pd(1)N$_4$B and Pd(2)N$_4$B rings adopt a boat conformation. Each of the palladium atoms essentially has a square-planar geometry. The four distances Pd−N [2.089(2), 2.098(2), 2.068(2) and 2.100(3) Å] are very similar and are in the range found for other Pd−N distances in polypyrazolylborate complexes [e.g., 2.113(3) and 2.079(2) Å in [PdPh{(pz)$_4$B-*N*,*N'*}(PPh$_3$)].[13] The bridging tetrakis(pyrazolyl)borate ligand forms chelate angles of 91.04(9) and 89.43(9)° at Pd(1) and Pd(2), respectively. The Pd−C_6F_5 distances [2.003(3), 2.006(6), 2.002(3), 2.005(3) Å] are in the range found in the literature.[23,24]

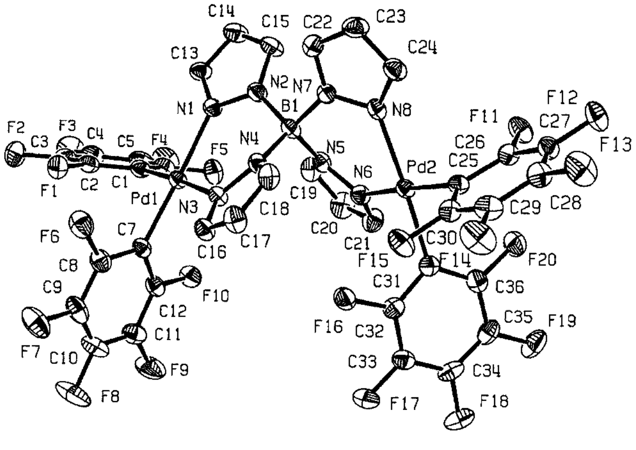


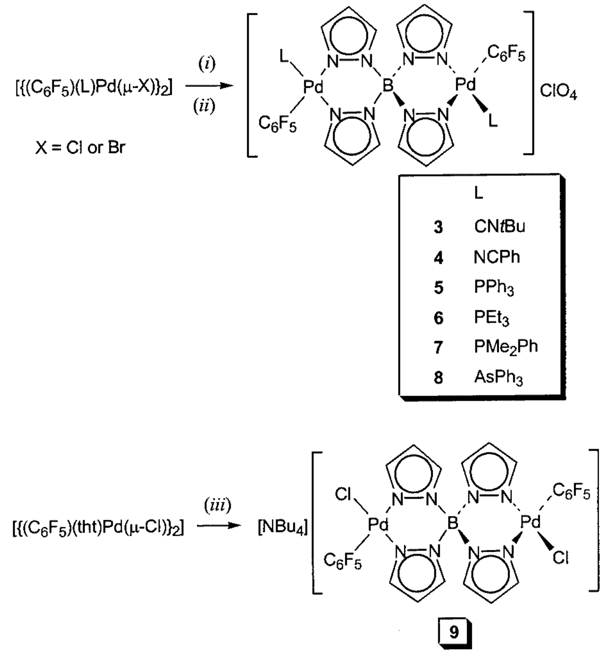
Figure 1. Structure of the anion of **1** showing the atom numbering scheme; hydrogen atoms have been omitted for clarity

Homodimetallic Complexes 3−9

The reaction of [{(C_6F_5)LPd(μ-X)}$_2$] (X = Cl, L = *t*BuNC, PhCN, PPh$_3$, AsPh$_3$; X = Br, L = PEt$_3$, PMe$_2$Ph) with AgClO$_4$ (1:2 molar ratio) in acetone, followed by the addition of K[B(pz)$_4$] (1:1 molar ratio) gives the corresponding dimetallic complexes **3**−**8** (Scheme 3). The reaction of [{(C_6F_5)LPd(μ-Cl)}$_2$] [L = tetrahydrothiophene (tht)] with K[B(pz)$_4$] and Bu$_4$NCl (1:1:1 molar ratio) leads to the formation of complex **9** (Scheme 3). In an acetone solution, complexes **3**−**9** behave as 1:1 electrolytes.[16]

Table 1. Selected bond lengths [Å] and angles [°] for complex **1**

Bond lengths		Bond angles	
Pd(1)−C(7)	2.003(3)	C(7)−Pd(1)−C(1)	85.13(12)
Pd(1)−C(1)	2.006(3)	C(7)−Pd(1)−N(3)	91.90(10)
Pd(1)−N(3)	2.089(2)	C(1)−Pd(1)−N(3)	177.00(11)
Pd(1)−N(1)	2.098(2)	C(7)−Pd(1)−N(1)	176.98(11)
Pd(2)−C(25)	2.002(3)	C(1)−Pd(1)−N(1)	91.93(11)
Pd(2)−C(31)	2.005(3)	N(3)−Pd(1)−N(1)	91.04(9)
Pd(2)−N(6)	2.068(2)	C(25)−Pd(2)−C(31)	86.73(12)
Pd(2)−N(8)	2.100(3)	C(25)−Pd(2)−N(6)	175.03(11)
		C(31)−Pd(2)−N(6)	90.49(11)
		C(25)−Pd(2)−N(8)	93.59(11)
		C(31)−Pd(2)−N(8)	176.64(11)
		N(6)−Pd(2)−N(8)	89.43(9)



	L
3	CN*t*Bu
4	NCPh
5	PPh3
6	PEt3
7	PMe2Ph
8	AsPh3

Scheme 3. (*i*) 2 $AgClO_4$; (*ii*) K[B(pz)$_4$]; (*iii*) K[B(pz)$_4$]/Bu_4NCl

The IR spectra of complexes **3−9** show an absorption at 790 cm^{-1} that is observed as a single band for the so-called X-sensitive mode,[20] as expected from the presence of only one C_6F_5 group in the coordination sphere of the palladium atom. Two absorptions at 1100 and 620 cm^{-1}, which are typical of the uncoordinated ClO_4^- (T_d) anion are observed for complexes **3−8**.[25] IR spectra of **3** and **4** also show an absorption assigned to ν(CN) at ca. 2230 cm^{-1} (*t*BuNC group[26−28] for **3**) or at 2280 cm^{-1} (PhCN ligand[28,29] for **4**). Complex **9** exhibits a Pd−Cl stretching vibration at 326 cm^{-1}.[30] The NMR spectroscopic data show that they exist in solution in a unique arrangement. Thus, the ^{19}F NMR spectra of **3−9** exhibit only one resonance for the *para*-fluorine atoms corresponding to only one type of pentafluorophenyl ring, and the ^{31}P NMR spectra of complexes **5−7** only show a resonance for the phosphane ligands. The ^{1}H NMR spectrum of complex **3** shows a singlet resonance for the *t*BuNC groups at δ = 1.56 ppm. On the other hand, the ^{1}H NMR spectra of complexes **3−9** exhibit two distinct sets of pyrazolyl signals of equal intensities, one assigned to the pyrazolyl group *trans* to C_6F_5 and the other to the pyrazolyl group *trans* to L (with three resonances 1:1:1 each). This suggests the occurrence of a very fast intramolecular interconversion between the conformational isomers that arises from the boat like M(N−N)$_2$B ring inversions of these compounds for which a spiro structure is expected. The resonances assigned to the pyrazolyl groups in the ^{1}H NMR spectrum of complex **3** are assigned by considering the NOE between the 3′-H and the *t*BuNC singlet, the usual criterion for pyrazoles where $^3J_{45} > {}^3J_{34}$,[21] and from two-dimensional ^{1}H-^{1}H COSY experiments. Furthermore, we have also performed ^{1}H-^{13}C COSY on **3** (Figure 2), and we have also found that the resonance assigned to the pyrazolyl C-3 CH carbon atoms is at a lower field than that of C-5.[22]

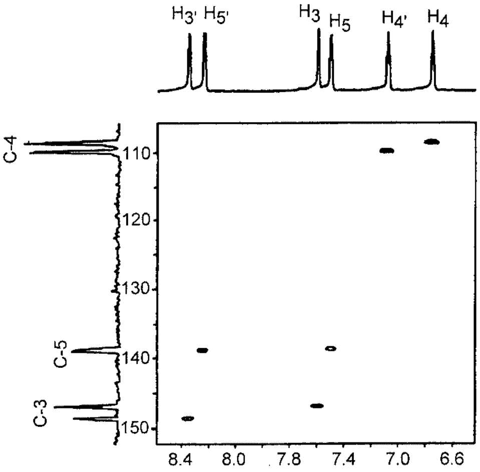


Figure 2. ^{1}H-^{13}C COSY of **3** in [D$_6$]acetone at 25 °C

The *ortho*- and *meta*-fluorine resonances of complexes **3−9** are duplicated, suggesting hindered rotation around the Pd−C_6F_5 bond.

The structure of **3** is shown in Figure 3 and selected bond lengths and angles in Table 2. The Pd(1)−N(2) bond length (*trans* to the C_6F_5 group) is longer (ca. 0.06 Å) than the Pd(1)−N(6) bond (*trans* to the *t*BuNC ligand), reflecting the stronger *trans* influence of the aryl group relative to the carbon donor group of the *t*BuNC ligand. The Pd−CN*t*Bu distances are very similar to those observed in the related complexes [{(C_6F_5)LPd(μ-X)}$_2$] (L = *t*BuNC; X = HNPh,[27] N=CPh$_2$ [26] and PhNNNPh[28]).

Monometallic Complexes 10−12

The reaction of [{(C_6F_5)(L)Pd(μ-X)}$_2$] (X = Cl, L = CN*t*Bu) with $AgClO_4$ (1:2 molar ratio) in acetone, followed by the addition of K[B(pz)$_4$] (1:2 molar ratio) gives the monometallic complex **10** (Scheme 4). The IR spectrum shows an absorption assigned to ν(CN) of the *t*BuNC group[26−28] at ca. 2230 cm^{-1}. The ^{19}F NMR spectrum at room temperature shows a unique set of sharp resonances, indicating the presence of only one type of C_6F_5 group.

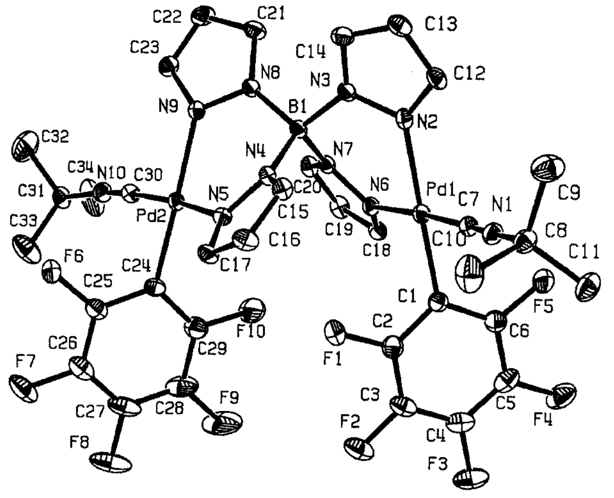
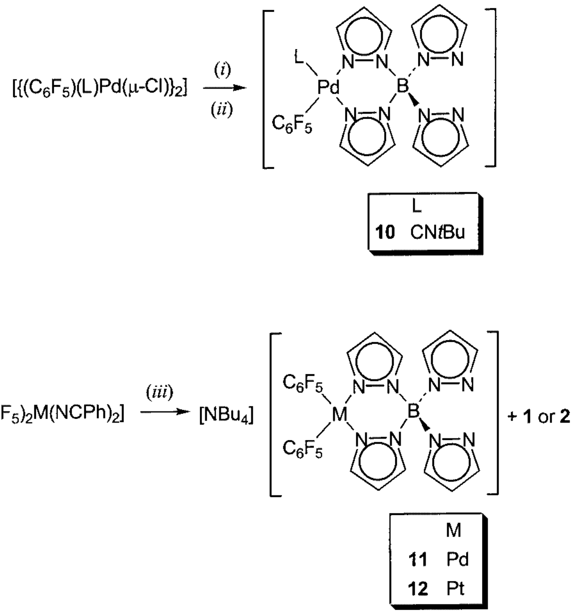


Figure 3. Structure of the cation of **3** showing the atom numbering scheme; hydrogen atoms have been omitted for clarity

Table 2. Selected bond lengths [Å] and angles [°] for complex **3**

Bond lengths		Bond angles	
Pd(1)−C(7)	1.946(4)	C(7)−Pd(1)−C(1)	87.59(16)
Pd(1)−C(1)	2.000(4)	C(7)−Pd(1)−N(6)	175.25(15)
Pd(1)−N(6)	2.026(3)	C(1)−Pd(1)−N(6)	90.71(14)
Pd(1)−N(2)	2.088(3)	C(7)−Pd(1)−N(2)	92.26(15)
Pd(2)−C(30)	1.931(4)	C(1)−Pd(1)−N(2)	179.44(15)
Pd(2)−C(24)	2.007(4)	N(6)−Pd(1)−N(2)	89.48(13)
Pd(2)−N(5)	2.026(3)	C(30)−Pd(2)−C(24)	84.46(17)
Pd(2)−N(9)	2.077(3)	C(30)−Pd(2)−N(5)	175.11(15)
		C(24)−Pd(2)−N(5)	91.42(15)
		C(30)−Pd(2)−N(9)	94.22(15)
		C(24)−Pd(2)−N(9)	178.54(15)
		N(5)−Pd(2)−N(9)	89.87(12)

However, in the ^{1}H NMR spectrum broad bands are observed due to exchanges between the four pyrazolyl groups. Fluxional motions of (η^2-BPz$_4$)palladium(II) complexes have been considered to involve the additional coordination of one uncoordinated pyrazolyl group near the palladium atom [via a tridentate tetrakis(pyrazolyl)borate−palladium structure], dissociation of one pyrazolyl group coordinated previously, and inversion of the boat-like six-membered Pd−(N−N)$_2$−B ring.[22] Variable-temperature ^{1}H NMR spectra of **10** have been recorded (Figure 4). At −60 °C the ^{1}H NMR spectrum exhibits eight different resonances in the pyrazolyl region with relative intensities of 1:2:1:1:1:2:1:3 (the two coordinated and the two uncoordinated pyrazolyl groups should all be nonequivalent, although casual overlaps of some signals are observed). The ^{1}H signals (nearly apparent triplets) at $\delta = 6.7-6.3$ are readily assigned to 4-H protons of the BPz$_4$ ligand. A singlet resonance is observed for the *t*BuNC group at $\delta = 1.6$ ppm.



Scheme 4. (*i*) 2 AgClO$_4$; (*ii*) 2 K[B(pz)$_4$]; (*iii*) 2 K[B(pz)$_4$]/2 nBu$_4$Cl

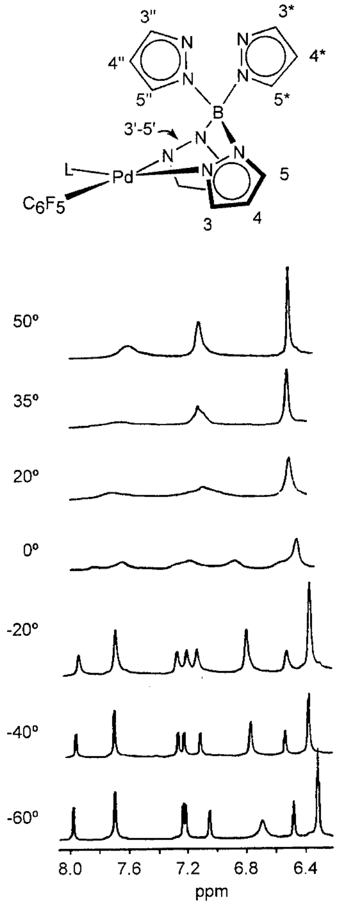


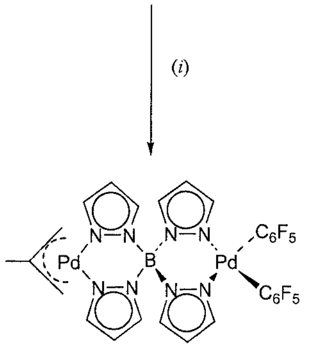
Figure 4. Temperature-dependent ^{1}H NMR (300 MHz) of pyrazolyl protons in **10** in [D$_6$]acetone

The reaction of *cis*-[(C$_6$F$_5$)$_2$M(NCPh)$_2$] (M = Pd or Pt) in CH$_2$Cl$_2$ with K[B(pz)$_4$] (pz = pyrazolyl) in a 1:1 molar ratio was attempted, in order to obtain the corresponding mononuclear complexes. However, mixtures containing both the dimetallic and the monometallic complexes **1** and **11** (for palladium), or **2** and **12** (for platinum), respectively, were obtained (Scheme 4). All attempts to separate them were unsuccessful.

Asymmetric Dinuclear Complex 13

The reaction of *cis*-[$(C_6F_5)_2Pd(NCPh)_2$] with the monomeric palladium tetrakis(pyrazol-1-yl)borate complex [$(\eta^3$-$CH_2CCH_3CH_2)Pd(\mu$-pz$)_2B($pz$)_2$][31] in a 1:1 molar ratio yields the asymmetric dinuclear complex **13** (Scheme 5).

[$(\eta^3$-$C_4H_7)Pd(\mu$-pz$)_2B($pz$)_2$]



13

Scheme 5

The new complex has been characterized on the basis of partial elemental analysis and spectroscopic data. A split absorption located at ca. 800 cm^{-1} in the IR spectrum is observed, which indicates that the *cis* arrangement[18,19] of the $Pd(C_6F_5)_2$ fragment is kept in the reaction. The ^1H NMR spectrum at room temperature shows the presence of three types of pz groups in a 2:1:1 ratio (Figure 5). No changes are observed in the temperature range −70 to + 50 °C. The ^{19}F NMR spectrum exhibits two resonances for the *para*-fluorine atoms, which is indicative of the existence of two different C_6F_5 rings. ^1H NMR resonances are assigned on the basis of a strong NOE between H_{syn} and 3*-H,[10] and selective decoupling experiments, and assuming that the 5′-H proton will be in a magnetic environment that is most similar to that of the 5*-H proton (Figure 5).[31,32] These findings are reconcilable with a structure where one ring is undergoing rapid inversion even at low temperatures, and the other is puckered in a boat conformation (Figure 5). Presumably, the puckered system is the $B(\mu$-pz$)_2Pd(\eta^3$-$CH_2CRCH_2)$ ring. The same pattern has been found previously in the *B,B*-bis(1-pyrazolyl)pyrazabole complexes [$(Et_2B(\mu$-pz$)_2B(\mu$-pz$)_2Pd(\eta^3$-$CH_2CRCH_2)$]$^+$ (R = Me or Ph).[31]

The structure of **13** has been established by X-ray diffraction and is shown in Figure 6 and selected bond lengths and angles in Table 3. Each of the palladium atoms essentially has a square-planar geometry. The Pd−N distances are very similar for Pd(1) and Pd(2), these values are similar to the distances found in polypyrazolylborate complexes of Pd^{II}.[13] The bridging tetrakis(pyrazolyl)borate ligand forms chelate angles of 88.9(2) and 88.7(2) Å at Pd(1) and Pd(2), respectively. The Pd(2)N_4B ring adopts a shallow boat conformation, the palladium and boron atoms are on the same side of the plane defined by the nitrogen atoms; in Pd(1)N_4B the boat is distorted giving a twist-like conformation.

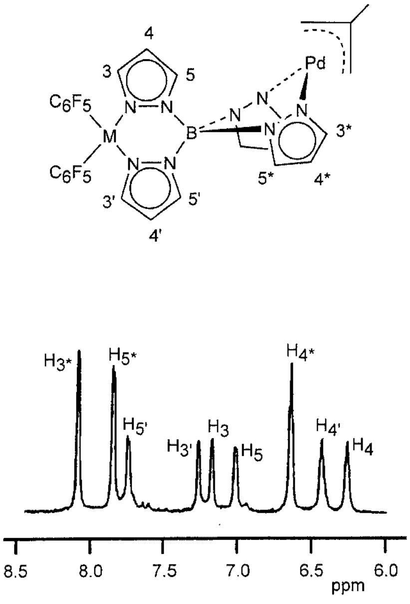


Figure 5. ^1H NMR (300 MHz) of pyrazolyl protons in **13** in [D_6]acetone

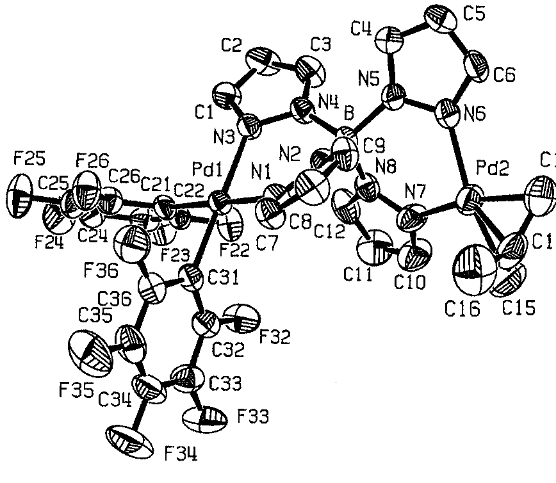


Figure 6. Structure of complex **13** showing the atom numbering scheme; hydrogen atoms have been omitted for clarity

The geometry of the allyl group is similar to that usually found in (η^3-allyl)palladium(II) complexes.[24,32] Thus, the allyl plane is not normal to the "Pd(1)N_2" plane, giving a dihedral angle of 114.5(5)°. The methyl group on the central carbon atom is 0.29(3) Å out of the allyl plane, on the same side as the Pd atom. The central carbon atom lies 0.55(1) Å to one side of the plane. The three carbon atoms bonded to the palladium atom are approximately equidistant from Pd [2.084(8), 2.121(7) and 2.127 (7) Å], and the carbon−carbon bond lengths of the η^3-allyl group are al-

Table 3. Selected bond lengths [Å] and angles [°] for complex **13**

Bond lengths		Bond angles	
Pd(1)−C(31)	2.013(6)	C(31)−Pd(1)−C(21)	85.2(2)
Pd(1)−C(21)	2.012(6)	C(31)−Pd(1)−N(1)	93.2(2)
Pd(1)−N(1)	2.081(5)	C(21)−Pd(1)−N(1)	176.6(2)
Pd(1)−N(3)	2.108(5)	C(31)−Pd(1)−N(3)	177.5(2)
Pd(2)−N(7)	2.056(6)	C(21)−Pd(1)−N(3)	92.8(2)
Pd(2)−C(15)	2.084(8)	N(1)−Pd(1)−N(3)	88.9(2)
Pd(2)−N(6)	2.099(5)	N(7) −Pd(2)−C(15)	101.1(3)
Pd(2)−C(13)	2.121(8)	N(7)−Pd(2)−N(6)	88.7(2)
Pd(2)−C(14)	2.127(8)	C(15)−Pd(2)−N(6)	169.1(3)
		N(7)−Pd(2)−C(31)	168.7(3)
		C(15)−Pd(2)−C(13)	67.8(4)
		N(6)−Pd(2)− C(13)	102.1(3)
		N(7)−Pd(2)−C(14)	132.9(3)
		C(15)−Pd(2)−C(14)	38.7(3)
		N(6)−Pd(2)−C(14)	134.4(3)
		C(13)−Pd(2)−C(14)	38.5(3)

most equal [1.397(12), 1.401(12) Å]. The Pd−C(1) bond lengths [2.013(6) and 2.012(6) Å] are similar to the values observed in other (pentafluorophenyl)palladium complexes.[23,24]

Experimental Section

General Methods: Calcd. C, H, N analyses were performed with a Carlo Erba model EA 1108 microanalyzer. Decomposition temperatures were determined with a Mettler TG-50 thermobalance at a heating rate of 5 °C min^{-1}. Conductance measurements were performed in an acetone solution ($c \approx 5 \times 10^{-4}$ mol L^{-1}) with a Crison 525 conductimeter. The NMR spectra were recorded with a Bruker AC 200E (^{1}H) or Varian Unity 300 (^{1}H, ^{19}F) spectrometer, using $SiMe_4$ or $CFCl_3$ as standards, respectively. NOE difference spectra were recorded with the following acquisition parameters: spectral width 4000 Hz, acquisition time 2.5 s, pulse width 5 µs (45°), relaxation delay 10 s, irradiation power 35−251 L, number of scans 100. Infrared spectra were recorded with a Perkin−Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets. The compounds $[(C_6F_5)_2M(NCPh)_2]$ (M = Pd,[29] Pt[34]) and $[\{(C_6F_5)(L)Pd(\mu\text{-}Cl)\}_2]$ (L = PPh_3, tht, CN*t*Bu),[35,36] K[B(pz)$_4$][37] were prepared as described elsewhere.

Safety Note: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

$[Bu_4N][\{(C_6F_5)_2M\}_2(\mu\text{-}pz)_2B(\mu\text{-}pz)_2]$ [M = Pd (1) or Pt (2)]: K[B(pz)$_4$] (19.6 mg, 0.06 mmol), followed by $[Bu_4N]Cl$ (16.7 mg, 0.06 mmol) was added to a solution of $[(C_6F_5)_2M(NCPh)_2]$ (M = Pd or Pt) (0.12 mmol) in dimethylformamide (DMF) (5 mL) . The resulting solution was stirred for 30 min at room temperature. Addition of water caused the precipitation of a white solid, which was collected by filtration and air-dried. It was recrystallized from dichloromethane/hexane.

1: Yield 73%. $C_{52}H_{48}BF_{20}N_9Pd_2$ (1402): calcd. C 44.5, H 3.4, N 9.0; found C 44.1, H 3.3, N 8.9. M.p. 300 °C (dec.). Λ_M = 84 S cm^2 mol^{-1}. IR (nujol): $\tilde{\nu}$ = 794, 784 cm^{-1} (Pd−C_6F_5). ^{1}H NMR ([D$_6$]acetone, TMS): δ = 7.75 (d, J_{45} = 2.5 Hz, 4 H, 5-H,), 7.23 (d, J_{34} = 1.4 Hz, 4 H, 3-H), 6.42 (pseudo-t, 4 H, 4-H) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone, TMS): δ = 145.7 (C-3), 138.2 (C-5), 107.6 (C-4) ppm. ^{19}F NMR ([D$_6$]acetone, $CFCl_3$): δ = −114.7 (m, 8 F_o), −163.7 (t, 4 F_p, J_{mp} = 19.7 Hz), −165.4 (m, 8 F_m) ppm.

2: Yield 77%. $C_{52}H_{48}BF_{20}N_9Pt_2$ (1580): calcd. C 39.5, H 3.1, N 8.0; found C 39.1, H 3.2, N 7.7. M.p. 288 °C (dec.). Λ_M = 86 S cm^2 mol^{-1}. IR (nujol): $\tilde{\nu}$ = 806, 798 cm^{-1} (Pt−C_6F_5). ^{1}H NMR ([D$_6$]acetone, TMS): δ = 7.73 (d, J_{45} = 2.5 Hz, 4 H, 5-H), 7.33 (d, J_{34} = 1.7 Hz, J_{HPt} = 10 Hz, 4 H, 3-H), 6.29 (pseudo-t, 4 H, 4-H) ppm. ^{19}F NMR ([D$_6$]acetone, $CFCl_3$): δ = −118.4 (d, J_{om} = 25.9 Hz, J_{PtF_o} 456 Hz, 8 F_o), −163.7 (t, J_{mp} = 19.7 Hz, 4 F_p), −165.3 (m, 8 F_m) ppm.

$[\{(C_6F_5)(L)Pd\}_2(\mu\text{-}pz)_2B(\mu\text{-}pz)_2]ClO_4$ [L = CN*t*Bu (3), NCPh (4), PPh$_3$ (5), PEt$_3$ (6), PMe$_2$Ph (7), AsPh$_3$(8): $AgClO_4$ (53.0 mg, 0.26 mmol) was added to a solution of $[\{(C_6F_5)(L)Pd(\mu\text{-}X)\}_2]$ (X = Cl, L = CN*t*Bu, PhCN, PPh_3, $AsPh_3$; X = Br, L = PEt_3, PMe_2Ph) (0.13 mmol) in acetone (15 mL). The solution was stirred at room temperature for 30 min, while it was protected from light. The white AgCl was then filtered off. K[B(pz)$_4$] (40.0 mg, 0.13 mmol) was then added to the resulting solution. The solution was stirred for 30 min at room temperature and concentrated under vacuum. The addition of ether/hexane caused the precipitation of a white solid, which was collected by filtration and air-dried. The complexes were recrystallized from dichloromethane/hexane.

3: Yield 80%. $C_{34}H_{30}BClF_{10}N_{10}O_4Pd_2$ (1092): calcd. C 37.4, H 2.8, N 12.8; found C 37.1, H 2.6, N 12.8. M.p. 157 °C (dec.). Λ_M = 117 S cm^2 mol^{-1}. IR (nujol): $\tilde{\nu}$ = 2234 cm^{-1} [ν(CN)], 798 cm^{-1} (Pd−C_6F_5 str). ^{1}H NMR ([D$_6$]acetone, TMS): δ = 8.34 (d, $J_{3'4'}$ = 1.6 Hz, 2 H, 3′-H), 8.23 (d, $J_{4'5'}$ = 2.6 Hz, 2 H, 5′-H), 7.39 (d, J_{34} = 1.6 Hz, 2 H, 3-H), 7.30 (d, J_{45} = 2.6 Hz, 2 H, 5-H), 6.87 (pseudo-t, 2 H, 4′-H), 6.55 (pseudo-t, 2 H, 4-H), 1.56 (s, 18 H, *t*BuNC) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone, TMS): δ = 148.5 (C-3′), 146.7 (C-3), 138.8 (C-5′), 138.6 (C-5), 109.7 (C-4′), 108.5 (C-4), 30.1 (*Me*$_3$C) ppm. ^{19}F NMR ([D$_6$]acetone, $CFCl_3$): δ = −119.1 (m, 4 F_o), −159.6 (t, 2 F_p, J_{mp} = 19.7 Hz), −163.6 (m, 4 F_m) ppm.

4: Yield 81%. $C_{38}H_{22}N_{10}BClF_{10}O_4Pd_2$ (1132): calcd. C 40.3, H 2.0, N 12.4; found C 39.9, H 1.8, N 12.4. M.p. 122 °C (dec.). Λ_M = 125 S cm^2 mol^{-1}. IR (nujol): $\tilde{\nu}$ = 2280 cm^{-1} [ν(CN)], 798 cm^{-1} (Pd−C_6F_5 str). ^{1}H NMR ($CDCl_3$, TMS): δ = 8.07 (unresolved d, 4 H, 3′-H + 5′-H), 7.72 (m, 4 H_m + 2 H_p), 7.57 (m, 4 H_o), 7.10 (m, 4 H, 3-H + 5-H), 6.87 (pseudo-t, 2 H, 4′′-H), 6.43 (pseudo-t, 2 H, 4-H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ = −121.1 (m, 2 F_o, J_{om} = 25.9 Hz), −122.5 (m, 2 F_o, J_{om} = 29.0 Hz), −157.4 (t, 2 F_p, J_{mp} = 19.7 Hz), −162.0 (m, 4 F_m) ppm.

5. Yield 84%. $C_{60}H_{42}BClF_{10}O_4N_8P_2Pd_2$ (1450): calcd. C 49.7, H 2.9, N 7.7; found C 49.4, H 2.8, N 7.6. M.p. 278 °C (dec.). Λ_M = 106 S cm^2 mol^{-1}. IR (nujol): $\tilde{\nu}$ = 796 (Pd−C_6F_5 str). ^{1}H NMR ([D$_6$]acetone, TMS): δ = 7.83 (unresolved d, 2 H, 3′-H), 7.5 (m, 34 H, PPh_3 + 2 5′-H + 2 × 3-H), 7.09 (unresolved d, 2 H, 5-H), 6.67 (unresolved pseudo-t, 2 H, 4′-H), 6.48 (unresolved pseudo-t, 2 H, 4-H) ppm. ^{19}F NMR ([D$_6$]acetone, $CFCl_3$): δ = −117.9 (m, 4 F_o), −160.1 (t, 2 F_p, J_{mp} = 19.7 Hz), −161.2 (m, 2 F_m), −161.9 (m, 2 F_m) ppm. ^{31}P NMR ([D$_6$]acetone, H_3PO_4): δ = 30.9 (s) ppm.

6: Yield 75%. $C_{36}H_{42}N_8BClF_{10}O_4P_2Pd_2$ (1162): calcd. C 37.2, H 3.6, N 9.6; found C 36.9, H 3.8, N 9.8. M.p. 271 °C (dec.). Λ_M = 110 S cm^2 mol^{-1}. IR (nujol): $\tilde{\nu}$ = 800 cm^{-1} (Pd−C_6F_5 str). ^{1}H NMR ([D$_6$]acetone, TMS): δ = 8.22 (unresolved d, 2 H, 3′-H), 8.03 (unresolved m, 2 H, 3-H), 7.32 (unresolved d, 2 H, 5′-H), 7.19 (unresolved d, 2 H, 5-H), 6.76 (unresolved pseudo-t, 2 H, 4′-H), 6.57 (unresolved m, 2 H, 4-H), 1.8 (m, 12 H, CH_2P), 1.1 (m, 18 H,

$C\mathit{H_3}CH_2P$) ppm. ^{19}F NMR ([D$_6$]acetone, $CFCl_3$): δ = −117.4 (m, 4 F_o), −159.3 (t, J_{mp} = 19.7 Hz, 2 F_p), −161.7 (m, 2 F_m), −162.3 (m, 2 F_m) ppm. ^{31}P NMR ([D$_6$]acetone, H_3PO_4): δ = 29.7 (s) ppm.

7: Yield 84%. $C_{40}H_{34}BClF_{10}N_8O_4P_2Pd_2$ (1202): calcd. C 40.0, H 2.9, N 9.3; found C 39.6, H 3.1, N 9.1. M.p. 244 °C (dec.). Λ_M = 115 S cm^2 mol^{-1}. IR (nujol): $\tilde{\nu}$ = 792 cm^{-1} (Pd−C_6F_5 str). ^1H NMR ([D$_6$]acetone, TMS): δ = 7.95 (unresolved m, 2 H, 3-H), 7.83−7.73 (m, 4 H, Ph), 7.65 (unresolved d, 2 H, 5′-H), 7.60−7.54 (m, 8 H, Ph + 2 × 3′-H), 7.36 (unresolved d, 2 H, 5-H), 6.71 (unresolved pseudo-t, 2 H, × 4′-H), 6.61 (unresolved m, 2 H, 4-H), 1.64 (d, J_{HP} = 19.5 Hz, 6 H, Me), 1.57 (d, J_{HP} = 19.6 Hz, 6 H, Me) ppm. ^{19}F NMR ([D$_6$]acetone, $CFCl_3$): δ = −117.9 (m, 2 F_o), −118.3 (m, 2 F_o), −159.6 (t, 1 F_p, J_{mp} = 20.0 Hz), −161.9 (m, 2 F_m), −162.5 (m, 2 F_m) ppm. ^{31}P NMR ([D$_6$]acetone, H_3PO_4): δ = 6.49 (s) ppm.

8: Yield 77%. $C_{60}H_{42}As_2BClF_{10}N_8O_4Pd_2$ (1538): calcd. C 46.7, H 2.7, N 7.3; found C 49.8, H 3.6, N 6.4. M.p. 213 °C (dec.). Λ_M = 120 S cm^2 mol^{-1}. IR (nujol): $\tilde{\nu}$ = 796 cm^{-1} (Pd−C_6F_5 str). ^1H NMR ([D$_6$]acetone, TMS): δ = 7.94 (d, $J_{4'5'}$ = 2.4 Hz, 2 H, 5′-H), 7.62 (unresolved d, 2 H, 3′-H), 7.5−7.3 (m, 32 H, $AsPh_3$ and 5-H), 7.27 (unresolved d, 2 H, 3-H), 6.69 (pseudo-t, 2 H, 4′-H), 6.55 (pseudo-t, 2 H, 4-H) ppm. ^{19}F NMR ([D$_6$]acetone, $CFCl_3$): δ = −117.0 (m, 4 F_o), −159.2 (t, J_{mp} = 19.7 Hz, 2 F_p), −160.7 (m, 2 F_m), −161.2 (m, 2 F_m).

$[Bu_4N][\{(C_6F_5)(Cl)Pd\}_2(\mu\text{-}pz)_2B(\mu\text{-}pz)_2]$ (9): K[B(pz)$_4$] (32.0 mg, 0.10 mmol), followed by [Bu$_4$N]Cl (29.6 mg, 0.10 mmol) was added to a solution of $[\{(C_6F_5)LPd(\mu\text{-}Cl)\}_2]$ [L = tetrahydrothiophene (tht)] (80.0 mg, 0.10 mmol) in acetone (15 mL).The resulting solution was stirred for 30 min at room temperature and concentrated under vacuum. The addition of ethanol/water caused the precipitation of a yellow solid, which was collected by filtration and air-dried. Yield 84%. $C_{40}H_{48}BCl_2F_{10}N_9Pd_2$ (1139): calcd. C 42.2, H 4.3, N 11.1; found C 41.8, H 4.0, N 11.2. M.p. 246 °C (dec.). Λ_M = 90 S cm^2 mol^{-1}. IR (nujol): $\tilde{\nu}$ = 796 cm^{-1} (Pd−C_6F_5 str), 326 cm^{-1} [ν(Pd−Cl)]. ^1H NMR ([D$_6$]acetone, TMS): δ = 8.43 (d, $J_{3'4'}$ = 1.6 Hz, 2 H, 3′-H), 7.95 (d, $J_{4'5'}$ = 2.6 Hz, 2 H, 5′-H), 7.35 (d, J_{34} = 1.6 Hz, 2 H, 3-H), 7.15 (d, 2 H, 5-H, J_{45} = 2.6 Hz), 6.60 (pseudo-t, 2 H, 4′-H), 6.37 (pseudo-t, 2 H, 4-H) ppm. ^{19}F NMR ([D$_6$]acetone, $CFCl_3$): δ = −118.7 (m, 4 F_o), −163.9 (t, 2 F_p, J_{mp} 19.7 Hz), −166.1 (m, 4 F_m) ppm.

$[(C_6F_5)(CN\mathit{t}Bu)Pd(\mu\text{-}pz)_2B(pz)_2]$ (10): $AgClO_4$ (46.0 mg, 0.20 mmol) was added to a solution of $[\{(C_6F_5)(\mathit{t}BuNC)Pd(\mu\text{-}Cl)\}_2]$ (80.0 mg, 0.10 mmol) in acetone (15 mL). The solution was stirred at room temperature for 30 min, while it was protected from light. The white AgCl was then filtered off. K[B(pz)$_4$] (64.8 mg, 0.20 mmol) was then added to the resulting solution. The solution was stirred for 30 min at room temperature and concentrated under vacuum. The addition of ether/hexane caused the precipitation of a white solid, which was collected by filtration and air-dried. The complex was recrystallized from dichloromethane/hexane. Yield 90%. $C_{23}H_{21}BF_5N_9Pd$ (636): calcd. C 43.5, H 3.3, N 19.8; found C 43.8, H 3.5, N 19.8. M.p. 182 °C (dec.). IR (nujol): $\tilde{\nu}$ = 2230 cm^{-1} [ν(CN)], 796 (Pd−C_6F_5 str). ^1H NMR ([D$_6$]acetone, TMS, 20 °C): δ = 7.7 (br, 3 H), 7.0 (br, 5 H), 6.3 (br, 4 H). ^1H NMR ([D$_6$]acetone, TMS, −60 °C): δ = 7.98 (d, J = 1.8 Hz, 1 H), 7.69 (unresolved d, 2 H), 7.23 (d, J = 2.4 Hz, 1 H), 7.21 (d, J = 2.1 Hz, 1 H), 7.05 (d, J = 2.4 Hz, 1 H), 6.69 (br, 2 H), 6.48 (pseudo-t, 1 H), 6.31 (pseudo-t, 3 H), 1.6 (s, 18 H, *t*BuNC) ppm. ^{19}F NMR ([D$_6$]acetone, $CFCl_3$, 20 °C): δ = −117.2 (m, 2 F_o), −159.7 (t, 1 F_p, J_{mp} 20.3 Hz), −163.5 (m, 4 F_m) ppm.

$[(C_6F_5)_2Pd(\mu\text{-}pz)_2B(\mu\text{-}pz)_2Pd(\eta^3\text{-}C_4H_7)]$ (13): $[(C_6F_5)_2Pd(NCPh)_2]$ (88.0 mg, 0.14 mmol) was added to a solution of $[(\eta^3\text{-}CH_2CCH_3CH_2)Pd(\mu\text{-}pz)_2B(pz)_2]$ (60.0 mg, 0.14 mmol) in acetone (10 mL). The resulting solution was stirred for 30 min at room temperature and concentrated under vacuum. The addition of ethanol/water caused the precipitation of a white solid, which was collected by filtration and air-dried. Yield 88%. $C_{28}H_{19}F_{10}N_8Pd_2$ (870): calcd. C 38.2, H 2.2, N 12.7; found C 38.2, H 2.3, N 12.5. M.p. 185 °C (dec.). IR (nujol): $\tilde{\nu}$ = 782, 808 (Pd−C_6F_5 str) cm^{-1}. ^1H NMR ([D$_6$]acetone, TMS): δ = 8.06 (unresolved d, 2 H, 3*-H), 7.82 (d, J_{4*5*} = 2.4 Hz, 2 H, 5*-H), 7.72 (d, $J_{4'5'}$ = 2.2 Hz, 1 H, 5′-H), 7.26 (unresolved d, 1 H, 3-H), 7.22 (unresolved d, 1 H, 3-

Table 4. Crystal structure determination details

	1	**3**	**13**
Empirical formula	$C_{52}H_{48}BF_{20}N_9Pd_2$	$C_{46}H_{32}BCl_3F_{10}N_8O_4Pd_2$	$C_{29}H_{21}BCl_2F_{10}N_8Pd_2$
Formula mass	1402.60	1176.67	966.05
Crystal system	monoclinic	monoclinic	triclinic
Unit cell dimensions			
a [Å]	9.2970(10)	14.2510(10)	11.8552(12)
b [Å]	17.1590(10)	17.9360(10)	12.8142(10)
c [Å]	35.642(3)	17.5860(10)	13.1023(10)
α [°]	90	90	89.809(5)
β [°]	93.510(10)	95.350(10)	64.431(6)
γ [°]	90	90	73.584(6)
Unit cell volume [Å^3]	5675.2(8)	4475.5(5)	1706.0(3)
Temperature [K]	173(2)	173(2)	298(2)
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
Z	4	4	2
μ [mm^{-1}]	0.744	1.075	1.301
Reflections collected	11161	9865	6870
Independent reflections	9959	7851	5933
R(int)	0.0278	0.0247	0.0313
$R1$ [$I > 2\sigma(I)$][a]	0.0309	0.0368	0.0508
wR_2 (all data)[b]	0.0779	0.0992	0.1206

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma\, w(F_o2)^2]^{0.5}$. [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

H), 7.02 (d, J_{45} = 2.4 Hz, 1 H, 5-H), 6.65 (unresolved pseudo-t, 2 H, 4*-H), 6.45 (unresolved pseudo-t, 1 H, 4′-H), 6.28 (unresolved pseudo-t, 1 H, 4-H), 4.04 (s, 2 H, H_{syn}), 3.23 (s, 2 H, H_{anti}), 2.12 (s, 3 H, CH_3) ppm. ^{19}F NMR ([D$_6$]acetone, $CFCl_3$): $\delta = -114.0$ (m, 4 F_o), −162.8 (m, 2 F_p), −164.7 (m, 4 F_m) ppm.

Determination of the X-ray Crystal Structures of 1, 3 and 13: Crystals of **1**, **3**·CH_2Cl_2 and **13**·CH_2Cl_2 suitable for X-ray diffraction studies were grown from dichloromethane/toluene/hexane solution, mounted on glass fibers, and transferred to the diffractometer (Siemens P4) as summarized in Table 4. Cell constants were refined from 82 (**1**), 57 (**3**) and 44 (**13**) reflections in the 2θ range of 9.5−25°. The structures were solved by direct methods (**1**, **13**) and by the Patterson method (**3**) using the SHELXS-97 program,[38] and refined anisotropically on F^2 (program SHELXL-97[38]). Hydrogen atoms were included using a riding model. CCDC-182373 (**1**), -182374 (**3**) and -182372 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK 9Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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