New palladium and platinum polyfluorophenyl complexes with pyrazolyl N-donor ligands. Analysis of the restricted rotation of the polyfluorophenyl rings

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The new N-donor chelate ligands bis(pyrazol-1-yl)(anisol-2-yl)methane, bpzmArOMe, bis(3,5-dimethylpyrazol-1-yl)hydrocarbylmethane (hydrocarbyl = anisol-2-yl, bpz*mArOMe; cyclohexyl, bpz*mCy) and bis(3,5-dimethylpyrazol-1-yl)ferrocenylmethane, bpz*mFec, have been prepared and characterized. New palladium and platinum polyfluorophenyl complexes were prepared with these ligands and those previously described: bis(pyrazol-1-yl)(phenol-2-yl)methane, bpzmArOH; bis(3,5-dimethylpyrazol-1-yl)(phenol-2-yl)methane, bpz*mArOH; 2-(pyrazol-1-yl)-pyridine, pzpy and 2-(pyrazol-1-yl)-pyrimidine, pzpm. For the bpzmR or bpz*mR complexes only one isomer has been found with the R group in an *axial* orientation. The fluxional behaviour of the new complexes, mainly the polyfluorophenyl rotation, has been analyzed. For the complexes with the nonplanar ligands, derived from bis(pyrazol-1-yl)methane, rotation of the pentafluorophenyl groups has been found to occur with different energy barriers. The presence of methyl groups in position 3 of the pyrazole rings reduces this barrier. The process is not affected by the presence of coordinating solvents or anions (Cl^-) or by a change in the complex concentration. For the derivative $Pd(2,3,4,6\text{-}C_6HF_4)_2$(pzpm), containing a planar ligand, two atropisomers are observed even at high temperature, which excludes the existence of polyfluorophenyl rotation. Processes of Pd–N bond rupture or *cis*,*trans*-isomerization have not been observed for this complex on the NMR time scale. The molecular structure of complex $Pd(C_6F_5)_2$(bpz*mFec) has been determined by an X-ray diffraction study.

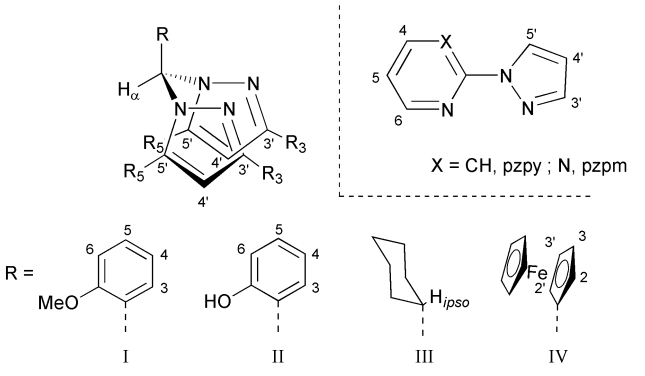
In recent years Pd(II) complexes bearing N-donor ligands[1] have received increasing attention. The reasons for this interest include the catalytic activity of these systems in the polymerization of alkenes,[2] alkene/CO copolymerization,[3] alkene/alkyl-acrylate copolymerization[4] and other catalytic processes[5] and also the study of important insertion reactions[6] or dynamic processes[7–9] carried out on complexes of this nature.

We have recently been working with two types of N-donor ligands derived from pyrazole: (i) compounds containing the bis(pyrazol-1-yl)methane backbone, which are consequently non-planar[9–11] [the groups of Canty,[12] Trofimenko,[13] Jordan[14] and Minghetti[15] have also prepared several types of palladium(II) bis(pyrazol-1-yl)methane derivatives] and (ii) systems with an approximately planar structure composed of two[16,17] or more[18,19] distinct heterocyclic moieties. Different properties of these compounds have been studied, with particular emphasis on catalytic applications[20] and fluxional behaviour that involves Pd–N bond rupture processes.[9,10,16–19] In the work described here, we have focused our attention on the synthesis of bis(polyfluorophenyl)palladium derivatives with these two types of N-donor ligands. The main goal of our work was to analyze the rotation of the polyfluorophenyl ring in the new metal complexes. Cases in which free[21,22] or restricted rotation[23,24] of polyfluorophenyl groups occurs in palladium or platinum complexes have been described in the literature. It is important to note that, in some cases, fluxional processes involving the ancillary ligands can produce mirror planes on the NMR time scale and give rise to an apparent aryl rotation[8,25,26] that could not actually occur. Clearly, when a real mirror plane coincides with the coordination plane the rotational process cannot be studied unless atropisomers are formed due to the presence of two (or more) polyfluorophenyl groups with an asymmetric substitution pattern.[19,21] In our complexes—with an appropriate choice of ligands—it would be possible to evaluate the influence of different factors that may be important for this polyfluorophenyl rotation: (i) the geometry of the ligand, whether planar or non-planar, (ii) the presence of methyl groups in the 3- and 5-positions of the pyrazole rings and (iii) the type of group present on the methynic carbon of the bis(pyrazolyl)methane backbone. For the complexes bearing bis(pyrazol-1-yl)Rmethane ligands it is also of interest to determine the orientation (axial or equatorial) of the R group at the methynic carbon and the factors that influence on the boat-to-boat equilibrium that could operate in these types of complexes.[10,12,27] The ligands used are indicated in Scheme 1.

Results and discussion

Synthesis of the ligands and complexes

The ligands bpzmArOH and bpz*mArOH have been reported previously.[28] The new ligands bpzmArOMe, **1**, bpz*mArOMe,



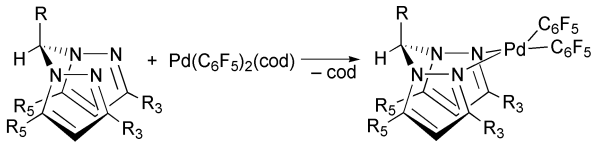
$R_3 = R_5 = H$, R = I, **1** (bpzmArOMe); R = II, bpzmArOH
$R_3 = R_5 = Me$, R = I, **2** (bpz*mArOMe); R = II, bpz*mArOH; R = III, **3** (bpz*m
R = IV, **4** (bpz*mFec)

Scheme 1

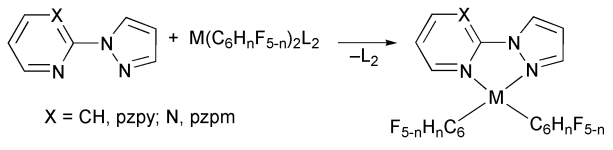
pz' = pyrazol-1-yl, R = anisol-2-yl, **1**
pz' = 3,5-Me_2-pyrazol-1-yl, R = anisol-2-yl, **2**
pz' = 3,5-Me_2-pyrazol-1-yl, R = cyclohexyl, **3**
pz' = 3,5-Me_2-pyrazol-1-yl, R = ferrocenyl , **4**

Scheme 2

2, bpz*mCy, **3** and bpz*mFec, **4**, were synthesized from the corresponding bis(pyrazol-1-yl)ketone derivatives and the aldehydes containing the R groups according to the procedure described by Peterson *et al.*[29] (see Scheme 2). The metal complexes were prepared by replacement of cod or THF ligands from the corresponding precursors (see Scheme 3). The products are stable in the solid state and in solution under an inert atmosphere. With the exception of complexes **6** and **8**, which are only sparingly soluble, the compounds are soluble in common polar solvents. The bpzmR complexes (**5** and **6**) are less soluble than those containing methylated bpz*mR ligands (**7**–**10**).



$R_3 = R_5 = H$, R = anisol-2-yl, $Pd(C_6F_5)_2$(bpzmArOMe), **5**
$R_3 = R_5 = H$, R = phenol-2-yl, $Pd(C_6F_5)_2$(bpzmArOH), **6**
$R_3 = R_5 = Me$, R = anisol-2-yl, $Pd(C_6F_5)_2$ (bpz*mArOMe), **7**
$R_3 = R_5 = Me$, R = phenol-2-yl, $Pd(C_6F_5)_2$ (bpz*mArOH), **8**
$R_3 = R_5 = Me$, R = cyclohexyl, $Pd(C_6F_5)_2$(bpz*mCy), **9**
$R_3 = R_5 = Me$, R = ferrocenyl, $Pd(C_6F_5)_2$(bpz*mFec), **10**



M = Pd, X = CH, L_2 = cod, n = 0, $Pd(C_6F_5)_2$(pzpy), **11**
M = Pd, X = N, L_2 = cod, n = 0, $Pd(C_6F_5)_2$(pzpm), **12**
M = Pt, X = N, L = THF, n = 0, $Pt(C_6F_5)_2$(pzpm), **13**
M = Pd, X = N, L_2 = cod, n = 1, $Pd(C_6HF_4)_2$(pzpm), **14**

Scheme 3

Characterization of the new derivatives

The new derivatives were characterized by elemental analysis, ^{1}H (Table 1), ^{13}C{^{1}H} (Table 2) and ^{19}F NMR (Table 3) and IR spectroscopy. The molecular structure of complex **10** was determined by X-ray diffraction. The IR spectra in the X–C_6F_5 sensitive region[30] (absorption at around 800 cm^{-1}) show one band for complexes **5**–**10**, a situation in accordance with the expected equivalence of the pentafluorophenyl groups. In contrast, complexes **11**–**14** give rise to two bands, which is in accordance with the asymmetry of the planar ligands.

The assignment of the NMR resonances was made by considering the chemical shifts and coupling constants[31] expected for the different atoms. In some cases, the information obtained from ^{1}H–^{1}H and ^{1}H–^{13}C COSY and NOE spectra was also taken into account. For complexes **5**–**10** (bpzmR or bpz*mR derivatives) signals corresponding to one type of N-donor ligand with equivalent pyrazolyl groups were found. In general, the resonances are shifted to lower field after coordination to the metal (positive CIS, coordination induced shift, $CIS = \delta_{complex} - \delta_{ligand}$). However, the protons situated near the metal centre give rise to negative CIS values. This fact must be due to the current anisotropy of the pentafluorophenyl rings,[32] an effect previously observed with other aromatic rings[33] as well as with polyfluorophenyl groups.[19]

In principle, two types of isomers are possible for the bpzmR or bpz*mR complexes, depending on whether the R group is in an axial or equatorial orientation (see Scheme 4). A boat-to-boat process should interconvert these two isomers. In our complexes only one isomer is observed. For complex **5** we have also confirmed that only one isomer exists at low temperature (acetone-d_6, $-90\,^\circ$C). The identity of the isomer present in solution can be deduced from NOE spectra. The NOE between H_α and $Me_{5'}$ or $H_{5'}$ is only possible when the R group is in an axial orientation (see Scheme 4, conformation A). It is likely that the isomer with the R group in the equatorial disposition would lead to a high degree of steric hindrance between this substituent and the pyrazolyl rings, particularly with Me_5. This selectivity in the conformation of the N-donor ligand has also been observed in other palladium complexes with similar bpz*mR ligands.[11] However, it should be noted that an equatorial location for the methynic substituent has been found in other types of complexes.[34]

In some palladium derivatives containing the pzpm ligand coordinated to PdClMe, PdCl(COMe) and Pd(2-Me-allyl) moieties[16,17] we found that when a group of high *trans* influence is situated *trans* to the pyrimidine ring, the Pd–N(pm) bond opens easily and produces an H_4/H_6 interchange. The fact that these two protons give rise to narrow and separate NMR signals in the polyfluorophenyl derivatives **12**–**14** (even at 130 °C in 1,1′,2,2′-tetrachloroethane-d_2 for **14**) indicates that, as expected, the polyfluorophenyl groups have a smaller *trans* influence than the methyl, acyl or η^3-2-Me-allyl groups and that the Pd–N bond rupture must have a very high energy barrier.

^{19}F NMR spectra and polyfluorophenyl rotation

In the bpzmR or bpz*mR complexes (**5**–**10**) one resonance due to F_{para} is observed in each case, which indicates the existence of only one type of pentafluorophenyl ring. This is in accordance with the C_s symmetry already deduced from the ^{1}H and ^{13}C NMR spectra. As far as the F_{ortho} and the F_{meta} signals are concerned, one (**7**, **8** and **10**) or two (**5**, **6**, **9**) resonances were observed at room temperature for each type of fluorine. This indicates that at this temperature a situation involving free or restricted rotation, respectively, of the pentafluorophenyl ring with respect to the C–Pd bond exists. In order to observe the two signals separately and to detect the corresponding coalescence temperatures, a number of variable temperature

Table 1 ^{1}H NMR data for derivatives **1–14**. Coupling constants are given in Hz. d = doublet, m = multiplet, pt = pseudotriplet, s = singlet, br = broad

	Pyrazole				
	H_4'	H_3'/Me_3'	H_5'/Me_5'	H_α	R
1[a]	6.31 t	7.63 d $J_{3'-4'}=1.7$	7.38 d $J_{5'-4'}=2.4$	8.03 s	6.94 d $J_{6-5}=8.3$ (H_6); 6.95 td $J_{4-5}=7.3$, $J_{4-6}=0.9$ (H_4); 7.38 td $J_{3-5}=1.7$ (H_5); 6.89 dd $J_{3-4}=7.9$ (H_3); 3.78 s (OMe)
2[a]	5.83 s	2.20 s	2.10 s	7.68 s	6.89 d $J_{6-5}=8.1$ (H_6); 6.91 t $J_{4-5}=7.3$ (H_4); 7.31 td $J_{3-5}=1.7$ (H_5); 6.82 dd $J_{3-4}=7.6$, $J_{3-5}=1.7$ (H_3); 3.73 s(OMe)
3[a]	5.75 s	2.19 s	2.36 s	5.83 d $J_{H\alpha-Hipso}=11.0$	3.0 m (H_{ipso}); 2.17–0.85 br m (CH_2)
4[a]	5.76 s	2.30 s	2.19 s	7.52 s	4.08 s (C_5H_5); 4.54 s (H_2+H_2' Cp.) 4.20 s (H_3+H_3' Cp.)
5[a]	6.36 t	7.27 d $J_{3'-4'}=1.3$	7.79 d $J_{5'-4'}=2.7$	7.91 s	6.95 d $J_{6-5}=8.4$ (H_6); 7.26 t $J_{4-5}=7.6$ (H_4); 7.51 t (H_5); 8.10 d $J_{3-4}=7.9$ (H_3); 3.82 s (OMe)
6[b]	6.49 t	7.36 d $J_{3'-4'}=2.2$	8.38 dd $J_{5'-4'}=2.7$, $J_{5'-3'}=1.0$	8.60 s	6.95 dd $J_{6-5}=8.06$ (H_6); 7.05 t $J_{4-5}=7.7$ (H_4); 7.35 dt (H_5); 7.87 dt $J_{3-4}=7.06$ (H_3); 9.28 s (OH)
7[a]	5.92 s	1.92 s	2.45 s	7.47 s	7.01 d $J_{6-5}=8.3$ (H_6); 7.21 t $J_{4-5}=7.3$ (H_4); 7.54 ddd $J_{5-3}=1.9$ (H_5); 7.28 d $J_{3-4}=7.6$ (H_3); 3.73 s (OMe)
8[a]	5.89 s	1.90 s	2.45 s	7.50 s	6.91 d $J_{6-5}=7.8$ (H_6); 7.14 t $J_{4-5}=7.6$ (H_4); 7.38 tm (H_5); 7.24 d $J_{3-4}=7.8$ (H_3); 6.58 br s (OH)
9[a]	5.84 s	1.91 s	2.37 s	5.69 d $J_{H\alpha-Hipso}=11.2$	5.5 m (H_{ipso}); 2.26–0.75 br m (CH_2)
10[a]	5.93 s	1.88 s	2.58 s	7.85 s	4.22 s (C_5H_5); 4.32 s (H_2+H_2' Cp); 4.44 s (H_3+H_3' Cp)

					Pyridine or pyrimidine			
				Other groups	H_3	H_4	H_5	H_6
11[b]	6.87 pt $J_{4'-5'}=3.2$	7.67 d $J_{3'-4'}=1.9$	9.01 d		8.31 d $J_{3-4}=8.5$	8.39 pt $J_{4-6}=1.7$	7.54 pt $J_{5-6}=5.4$, $J_{5-4}=6.1$	7.98 d
12[b]	6.87 pt $J_{4'-5'}=3.2$	7.76 d $J_{3'-4'}=2.0$	8.89 dd		–	9.17 pt $J_{4-6}=2.1$	7.68 pt $J_{5-6}=5.5$, $J_{5-4}=4.9$	7.98 dd
13[b]	6.96 d $J_{4'-5'}=3.2$	7.94 d $J_{3'-4'}=1.9$	8.93 dd		–	9.26 dd $J_{4-6}=2.1$	7.69 t $J_{5-6}=5.6$, $J_{5-4}=4.7$	8.67 dd
14[b]	7.68 d[c]	6.87 m	8.86 m	6.66 m (C_6HF_4)	–	9.16 dd $J_{4-6}=2.1$, $J_{4-5}=4.8$	7.70 t	8.30 dd

[a] Chloroform-d. [b] Acetone-d_6. [c] Overlapped signals.

Table 2 $^{13}C\{^1H\}$ NMR data for derivatives **1–14**. Unless specified the signals are singlets. m = *meta*, o = *ortho*, p = *para*

	Pyrazole						
	C_3'	C_4'	C_5'	Me_3'	Me_5'	C_α	R
1[a]	140.6	105.9	129.3			73.1	156.6 (C_1); 124.1 (C_2); 110.8 (C_6); 120.7 (C_4); 130.8 (C_5); 127.8 (C_3); 55.6 (–OMe)
2[a]	147.8	140.1	106.3	13.8 or 11.3		69.8	110.7 (C_6); 120.6 (C_4); 129.9 (C_5); 128.5 (C_3); 55.8 (–OMe)
3[a]	147.4	106.2	139.7	13.6	11.4	76.7	39.5 (C_{ipso}); 26.2 (C_p); 29.4, 25.4 (C_o, C_m)
4[a]	147.3	106.4	139.9	13.6	11.9	72.3	68.9 (C_p); 68.2 ($C_{p2,2'}$); 69.5 ($C_{p3,3'}$)
5[b]	107.3	144.5	135.9			72.8	157.2 (C_1); 124.0 (C_2); 112.0 (C_6); 121.7 (C_4); 132.2 (C_5); 129.0 (C_3); 56.0 (–OMe)
6[b]	107.8	144.8	136.2			73.3	155.6 (C_1); 122.8 (C_2); 116.7 (C_6); 121.3 (C_4); 132.4 (C_5); 129.5 (C_3)
7[a]	153.3	108.3	141.8	14.4 or 12.0		66.7	117.7 (C_2), 111.6 (C_6); 122.7 (C_4); 131.8 (C_5); 130.1 (C_3)
8[a]	159.0	114.0	147.8	20.0 or 17.8		72.4	159.6 (C_1); 125.6 (C_2); 121.8 (C_6); 128.1 (C_4); 137.3 (C_5); 135.8 (C_3)
9[a]	152.9	108.3	143.9	13.9	11.6	73.6	43.0 (C_{ipso}); 26.5 (C_p); 29.0, 25.4 (C_o, C_m)
10[a]	153.7	108.6	140.6	14.4	12.2	69.2	69.3 (C_p); 68.3 ($C_{p2,2'}$); 69.5 ($C_{p3,3'}$)

				Pyridine or pyrimidine					
				C_2	C_3	C_5	C_4	C_6	Other groups
11[b]	144.5	111.3	131.3	150.3	113.4	124.8	150.0	143.2	
12[b]	145.8	111.6	132.2	155.3		121.7	162.3	159.3	
13[b]	133.3[c] $J_{C-Pt}=12.6$	112.3[c] $J_{C-Pt}=22.4$	158.9[c] $J_{C-Pt}=40.3$			122.5[c] $J_{C-Pt}=22.8$	162.0	146.1[c] $J_{C-Pt}=65.9$	
14[b]	145.8	112.0	122.1			122.2	162.5	159.9	100.3 [m $C_6HF_4(CH)$]

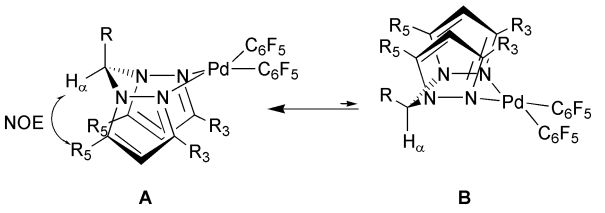
[a] Chloroform-d. [b] Acetone-d_6. [c] With platinum satellites.

Table 3 ^{19}F NMR data for complexes **5**–**14**. Coupling constants are given in Hz. br s = broad singlet, pd = pseudodoublet, m = multiplet, $F_m = F_{meta}$, $F_o = F_{ortho}$, $F_p = F_{para}$

	F_o	F_m	F_p
5[b]	−111.13 pd $J_{Fo\text{-}Fm} = 27.5$ −111.56 pd $J_{Fo\text{-}Fm} = 30.5$	−161.27 m −161.71 m	−159.30 t $J_{Fp\text{-}Fm} = 19.8$
6[a]	−103.89 pd $J_{Fo\text{-}Fm} = 27.5$ −104.44 pd $J_{Fo\text{-}Fm} = 27.5$	−154.16 m −154.58 m	−152.18 t $J_{Fp\text{-}Fm} = 19.8$
7[a]	−115 br s	−165.90 m	−163.09 t $J_{Fm\text{-}Fp} = 21.4$
8[a]	−115 br s	−165.96 m	−163.19 t $J_{Fm\text{-}Fp} = 19.8$
9[a]	−117.06 m −119.18 m	−167.93 m	−165.41 pt $J_{Fm\text{-}Fp} = 19.8$
10[a]	−113.38 m	−165.70 m	−162.88 t $J_{Fm\text{-}Fp} = 21.4$
11[a]	−117.20 m −117.41 m	−163.40 m −164.22 m	−160.79 t −160.18 t $J_{Fm\text{-}Fp} = 18.3$
12[a]	−117.26 m −117.59 m	−163.40 m −164.08 m	−160.27 t −160.83 t $J_{Fm\text{-}Fp} = 21.4$
13[b]	−120.69[d] m (4F)[c] $J_{Pt\text{-}F} = 457.8$	−167.22 m −167.65 m	−165.22[d] t $J_{Fm\text{-}Fp} = 21.3$; $J_{Pt\text{-}F} = 18.2$ −165.52[d] t $J_{Fm\text{-}Fp} = 21.3$; $J_{Pt\text{-}F} = 18.2$

	F_2	F_3	F_4	F_6
14[b]	−111.63 m (4F)	−170.90 m (2F) −171.23 m (2F)	−143.85 m (2F) −144.20 d ($J = 21.3$) −144.25 d ($J = 18.3$)	−92.05 m (4F)

[a] Chloroform-d. [b] Acetone-d_6. [c] Overlapped signals. [d] With platinum satellites.



Scheme 4

^{19}F NMR studies were carried out for **5** and **7** (chloroform-d) and for **6**, **9** and **10** (1,1′,2,2′-tetrachloroethane-d_2). The corresponding values of the free energy of activation and the respective coalescence temperatures obtained are collected in Table 4 and represented in Fig. 1. Values for the previously reported[11] complexes $Pd(C_6F_5)_2$(bpz*mR) (R = phenyl, **15**, and pyridin-2-yl, **16**; chloroform-d) have also been included for the sake of comparison. Complexes bearing methylated pyrazolyl groups (bpz*mR) have $\Delta G^{\ddagger}_c$ values that approximately fit a straight line, giving an indication of a similar energy barrier with a negligible influence of the R group. Unexpectedly the $\Delta G^{\ddagger}_c$ data for the two complexes with unmethylated pyrazole rings (**5** and **6**) are significantly higher. The effect of the substituents in the pyrazole ring is more evident upon comparing complexes **5** and **7**, both of which have R = anisol-2-yl and show similar coalescence temperatures. The $\Delta G^{\ddagger}_c$ value is significantly higher (*ca.* 11.3 kJ mol^{-1}) for the complex that contains the unmethylated ligand. The R groups that are more remote from the coordination sphere seem to have only a minor influence on the Pd–aryl rotation.

Table 4 Coalescence temperatures and free activation energies for the F_{ortho}–F_{ortho} exchange (Pd–C_6F_5 rotation) in $Pd(C_6F_5)_2$(bpz′mR) complexes from the variable temperature ^{19}F NMR spectra[a]

	T_c[b]/K	$\Delta G^{\ddagger}_c$[c]/kJ mol^{-1}
5[d]	301	65.2
6[e]	327	67.3
7[d]	298	53.9
9[e]	349	64.7
10[e]	273	52.1
15[d,f]	283	53.9
16[d,f]	311	57.1

[a] See Fig. 1 for representation. [b] Coalescence temperature. [c] Free activation energy at the coalescence temperature calculated by $\Delta G^{\ddagger}_c = aT[9.972 + \log(T_c/\delta\nu)]$ with $a = 1.914 \times 10^{-2}$. [d] Chloroform-d. [e] 1,1′,2,2′-tetrachloroethane-d_2. [f] Ref. 11.

The effect on this dynamic process of factors such as concentration, solvent or addition of coordinating anions (Cl^-) has also been studied. The results are the following: (i) the previously reported[11] $\Delta G^{\ddagger}_c$ values and coalescence temperatures for complexes **15** and **16** in acetone-d_6 fit within the experimental error with those calculated herein in chloroform-d; (ii) these parameters do not change with dilution of a chloroform-d solution of **16**, (iii) the addition of PPh_4Cl to a solution of **15** in chloroform-d does not modify the coalescence temperature or the $\Delta G^{\ddagger}_c$ data.

When mechanistic considerations are taken into account, rotation in the square planar complex[25] or in three-coordinate intermediates through dissociation of neutral[35] or anionic ligands[23] has been proposed. In our case, the negligible effect produced by a coordinating solvent or after the addition of chloride allows us to exclude the formation of three- or five-coordinate species. For positive effects of coordinating solvents or anions in dynamic processes where three- or five-coordinate intermediates are proposed see, for example, ref. 36 and 37. An intermolecular mechanism with the participation, for example, of the coordinating atoms of the R group can also be excluded because the process is not affected by dilution. We propose that the rotation takes place in the four-coordinate complexes. In principle, for rotation in a square planar geometry one would expect a smaller barrier with the ligands containing unmethylated pyrazole because these should impose less steric hindrance and the pentafluorophenyl groups would be able to rotate more freely. However, this hypothesis is not in agreement with our experimental data. Crystallographic Pd–N distances are not very sensitive to the substituent in position 3 of pyrazole when bpzm ligands are coordinated to the same PdX_2 fragment.[14] However, bulky substituents in this position produce a significant distortion in the boat metallacycle, reducing the PdNN/NNNN dihedral angle and also the bite angle of the N-donor ligand[14,38] (see Scheme 5). This distortion pushes away the X ligands from the aforementioned bulky substituent and opens the X–Pd–N angle. In our case, this distortion could facilitate the pentafluorophenyl rotation. In any case, theoretical studies could

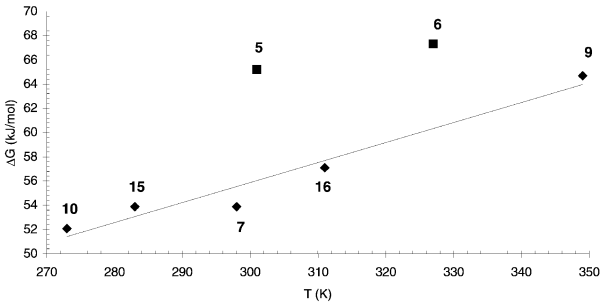
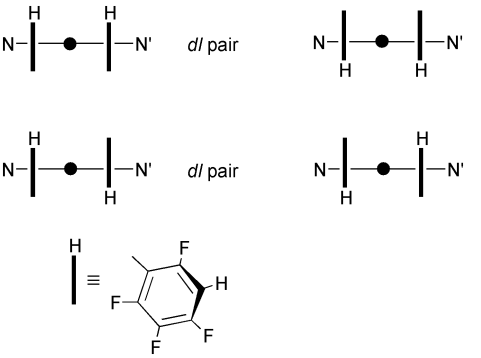


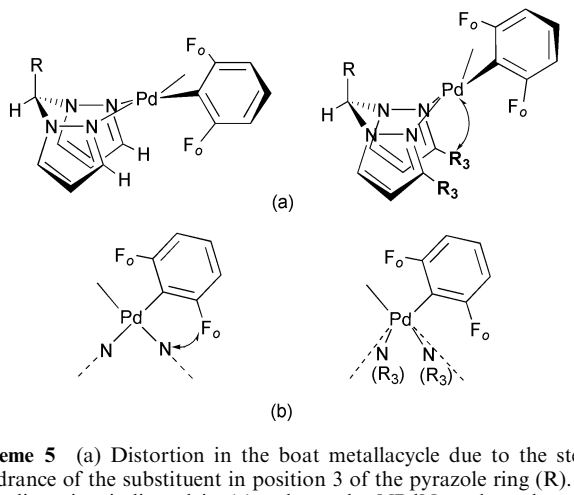
Fig. 1 Linear plot of $\Delta G^{\ddagger}_{c}$ (kJ mol^{-1}) *versus* T_c for the F_{ortho}–F_{ortho} exchange in $Pd(C_6F_5)_2$(bpz′mR) complexes (see Table 4 for values). Numbers near the symbols refer to the corresponding complexes: (◆) complexes bearing the methylated bpz*mR ligands; (■) complexes bearing non-methylated bpzmR ligands.



Scheme 6 Schematic view of the possible atropisomers for complex **14** considering an averaged perpendicular orientation of the C_6HF_4 groups.

help in understanding this unexpected effect of the pyrazole substituents.

^{19}F NMR data for the complexes with planar ligands **11**–**13** show, as expected, two types of pentafluorophenyl ring (two signals for F_{para}). Two signals each were also observed for the F_{ortho} (isochronous for **13**) and F_{meta} atoms. This does not constitute evidence of free rotation of the pentafluorophenyl groups because the coordination plane is a mirror plane. Due to this uncertainty we decided to synthesize a complex containing 2,3,4,6-C_6HF_4 rings that consisted of two different halves: Pd(2,3,4,6-C_6HF_4)$_2$(pzpm) (**14**). Free rotation of the polyfluorophenyl rings in this complex will give rise to two different resonances for each type of fluorine atom. However, in the case of restricted rotation one would expect two different atropisomers[19,21,35] (see Scheme 6), depending on the relative orientation of the hydrogen atoms situated in the 5-position. In this case, each type of fluorine atom will give rise to four resonances. In the ^{19}F NMR spectrum of **14** at room temperature in 1,1′,2,2′-tetrachloroethane-d_2, the resonances due to the F_4 atoms were the most informative. Four signals in a 1 : 1 : 1 : 1 ratio were observed for this fluorine. Such a pattern indicates that the two atropisomers, equally populated, do not interconvert at room temperature and, consequently, that the rotation of the C_6HF_4 rings is restricted. At 130 °C an identical pattern of four different F_4 signals was observed, which indicates that both polyfluorophenyl rotation and *cis-trans* isomerization are processes having very high energy barriers in **14**. Considering the result obtained with complex **14**, we believe that a restricted rotation also exists at room temperature for the pentafluorophenyl complexes with pzpy (**11**) or pzpm (**12**). We propose that in these complexes with planar ligands the high difference in steric hindrance between perpendicular or parallel disposition of the $C_6H_nF_{5-n}$ groups with respect to the coordination plane preclude the Pd–aryl rotation.



Scheme 5 (a) Distortion in the boat metallacycle due to the steric hindrance of the substituent in position 3 of the pyrazole ring (R). (b) The distortion indicated in (a) reduces the NPdN angle and consequently also the steric hindrance of the pyrazole N-donor atom with the C_6F_5 groups.

X-Ray structure of 10

Crystals of **10** belong to the monoclinic space group $P2_1/n$. An ORTEP plot of the molecule is shown in Fig. 2. The crystallographic data and a list of selected bond distances and angles are given in Tables 5 and 6, respectively. The geometry around the Pd(1) atom is approximately square planar with two coordinated pyrazole rings and two C_6F_5 groups. The bite angle N(22)–Pd(1)–N(12) [84.22(13)°] and that formed by the two C_6F_5 groups, C(61)–Pd(1)–C(51) [88.37(17)°], are smaller than 90°. More open angles C(51)–Pd(1)–N(22) [92.26(15)°] and C(61)–Pd(1)–N(12) [95.13(15)°] complete the square plane geometry. The bite angle is intermediate between those found in unsubstituted pyrazole or pyrazole substituted with bulky groups in position 3.[14] This fact may be in relation with the stated fluxional behaviour of these types of compounds. The respective Pd(1)–N and Pd(1)–C distances are comparable to those found in other bis(pyrazolyl)methane[11,14,15,39] and polyfluorophenyl Pd(II) complexes.[19,23,25] The coordination of the bpz*mFec ligand gives rise to a boat-like metallacycle,

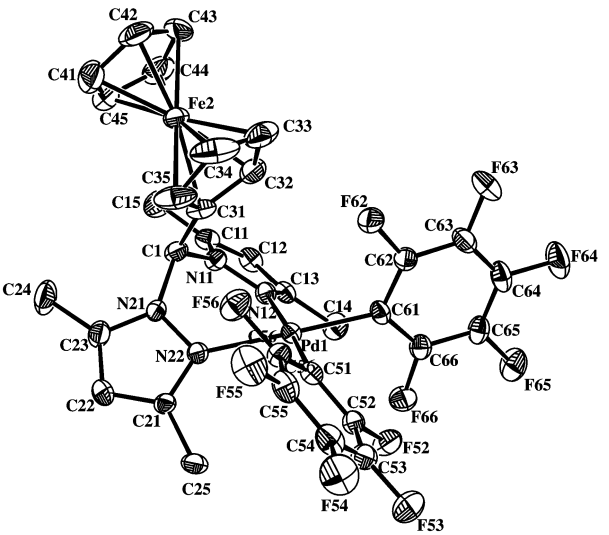


Fig. 2 ORTEP view with atomic numbering of **10** (30% probability ellipsoids).

Table 5 Crystal data and structure refinement for **10**

Empirical formula	$C_{33}H_{24}F_{10}FeN_4Pd$
Formula weight	828.81
Temperature/K	293(2)
Wavelength/Å	0.71070
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	12.8040(10)
b/Å	16.86(3)
c/Å	15.137(2)
β/°	105.41(4)
Volume/Å^3	3150(6)
Z	4
Abs. coef./cm^{-1}	11.22
Total reflect.	7576
Indep. reflect.	7576
R_{int}	0.0328
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0380$
	$wR_2 = 0.0720$

$R_1 = \sum\|F_o| - |F_o\| \,/\, \sum |F_o|$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] \,/\, \sum [w(F_o^2)^2]]^{0.5}$.

Table 6 Selected bond lengths (Å) and angles (deg) for **10**

Pd(1)–N(12)	2.131(5)	C(61)–Pd(1)–C(51)	88.37(17)
Pd(1)–N(22)	2.094(3)	C(61)–Pd(1)–N(22)	179.11(16)
Pd(1)–C(51)	2.025(6)	C(51)–Pd(1)–N(22)	92.26(15)
Pd(1)–C(61)	2.018(4)	C(61)–Pd(1)–N(12)	95.13(15)
C(1)–N(11)	1.452(5)	C(51)–Pd(1)–N(12)	176.15(15)
C(1)–N(21)	1.465(5)	N(22)–Pd(1)–N(12)	84.22(13)
C(1)–C(31)	1.506(6)	N(11)–C(1)–N(21)	110.3(3)
		N(11)–C(1)–C(31)	113.7(4)
		N(21)–C(1)–C(31)	113.3(4)

Pd(1)–N(12)–N(11)–C(1)–N(21)–N(22), with the ferrocenyl group attached to the carbon atom in an axial position. This is in agreement with the data obtained for the complex in solution. The ferrocenyl unit adopts a orientation that minimizes the possible steric repulsions with the $Pd(C_6F_5)_2$ fragment, having the unsubstituted Cp group pointing away from the pentafluorophenyl groups.

Conclusions

Square planar complexes of Pd(II) and Pt(II) have been prepared through the coordination of planar and non-planar chelate N-donor ligands to $Pd(C_6F_5)_2$, $Pd(2,3,4,6\text{-}C_6HF_4)_2$ or $Pt(C_6F_5)_2$ fragments. For the complexes with a bis(pyrazol-1-yl)methane (bpz*mR) backbone only one isomer is formed with the R groups in an axial disposition and no boat-to-boat inversion has been found. Different energetic barriers have been measured on the NMR time scale for the Pd–polyfluorophenyl rotation. For the complexes with non-planar ligands, the process is not affected by the presence of a coordinating solvent or anion (Cl^-) or a change in the complex concentration. These facts exclude the participation of three- or five-coordinate intermediates and we propose that the rotation occurs *via* four-coordinate species. Unexpectedly, the presence of Me substituents in the position adjacent to the N-donor atoms facilitates the rotation. The presence of more remote groups, even those with coordinating ability, seems to have less of an effect on the Pd–polyfluorophenyl rotation. The rigidity observed, even at high temperature, for complex $Pd(2,3,4,6\text{-}C_6HF_4)_2$(pzpm), both in ^{1}H and ^{19}F NMR indicates that Pd–N bond rupture, *cis-trans* isomerization and Pd–polyfluorophenyl rotation are high-energy processes, falling outside of the NMR time scale. This could be extrapolated to the other Pd complexes containing planar ligands (pzpy and pzpm) and contrast with the fluxional behaviour found in complexes with the non-planar ligands.

Experimental

General comments

All manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents and degassed before use. Elemental analyses were performed with a Thermo Quest FlashEA 1112 microanalyzer. IR spectra were recorded as KBr pellets or Nujol mulls with a Perkin–Elmer PE 883 IR spectrometer. ^{1}H, ^{13}C{^{1}H} and ^{19}F NMR spectra were recorded on a Varian Unity 300 spectrometer. Chemical shifts (ppm) are relative to TMS (^{1}H, ^{13}C NMR) and $CFCl_3$ (^{19}F). COSY spectra: standard pulse sequence, acquisition time 0.214 s, pulse width 10 μs, relaxation delay 1 s, 16 scans, 512 increments. The NOE difference spectra were recorded with 5000 Hz, acquisition time 3.27 s, pulse width 90°, relaxation delay 4 s, irradiation power 5–10 dB. For variable temperature spectra, the probe temperature (± 1 K) was controlled by a standard unit calibrated with a methanol reference. Free energies of activation were calculated[40] from the coalescence temperature (T_c) and the frequency difference between the coalescing signals (extrapolated at the coalescence temperature) ($\delta\gamma$) with the formula $\Delta G^{\ddagger}_c = aT\,[9.972 + \log(T/\delta\nu)]$ with $a = 1.914 \times 10^{-2}$. The estimated error in the calculated free energies of activation is ± 1.0–1.1 kJ mol^{-1}. $Pd(C_6F_5)_2$(cod), $Pt(C_6F_5)_2(THF)_2$ and $Pd(2,3,4,6\text{-}C_6HF_4)$ were prepared similarly to other polyfluorophenyl complexes.[41] Bis(pyrazol-1-yl)ketone and bis(3,5-dimethylpyrazol-1-yl)ketone were prepared according with reported methods.[29] Equally, bpzmArOH and bpz*mArOH were prepared according to the literature.[28] The aldehydes were purchased from Aldrich.

Synthesis of the new derivatives

bpz*mArOMe, 1. A mixture of bis(pyrazol-1-yl)ketone (500 mg, 3.08 mmol) and 420 mg (3.08 mmol) of *ortho*-anisaldehyde and $CoCl_2$ (*ca.* 14 mg) as catalyst is heated at 60 °C for 7 h. The product is extracted with 20 mL of CH_2Cl_2. The solution is washed with water to eliminate the $CoCl_2$ and the solution is dried with anhydrous $MgSO_4$. The solution is evaporated until dryness and the white solid of **1** is recrystallized from diethyl ether–pentane (1 : 10). Yield: 57%. Anal. calcd. for $C_{14}H_{14}N_4O$ (254.30): C, 66.13; H, 5.55; N, 22.03; found: C, 65.83; H, 5.38; N, 21.60.

bpz*mArOMe, 2. The method is similar to that used for derivative **1**. Amounts are as follows: 500 mg (2.29 mmol) of bis(3,5-dimethylpyrazol-1-yl)ketone and 312 mg (2.29 mmol) of *ortho*-anisaldehyde. A white solid is obtained. Yield: 60%. Anal. calcd. for $C_{18}H_{22}N_4O$ (310.37): C, 69.65; H, 7.14; N, 18.05; found: C, 69.23; H, 6.93; N, 17.54.

bpz*mCy, 3. Bis(3,5-dimethylpyrazol-1-yl)ketone (1.00 g, 4.58 mmol) and 981 mg (4.58 mmol) of ferrocenecarboxaldehyde are heated under reflux in 25 mL of toluene during 5 h. The solution is evaporated until dryness and the residue is recrystallized from diethyl ether–pentane (1 : 10). Brown-red crystals of **3** are obtained. Yield: 78%. Anal. calcd. for $C_{17}H_{26}N_4$ (286.41): C, 71.29; H, 9.15; N, 19.56; found: C, 71.17; H, 9.08; N, 19.72.

bpz*mFec, 4. The method is similar to that used for **3**. Amounts are as follows: 500 mg (2.29 mmol) of bis(3,5-dimethylpyrazol-1-yl)ketone and 0.276 mL (2.29 mmol) of

cyclohexanecarboxaldehyde. The oily residue obtained after the solvent evaporation becomes a white solid after 3 days. Yield: 60%. Anal. calcd. for $C_{21}H_{24}N_4Fe$ (388.29): C, 64.96; H, 6.23; N, 14.43; found: C, 65.02; H, 6.42; N, 14.21.

Pd(C_6F_5)$_2$(bpzmArOMe), 5. Pd(C_6F_5)$_2$(cod) (100 mg, 0.18 mmol) is dissolved in 20 mL of acetone and 46 mg (0.18 mmol) of bpzmArOMe are added. The solution is stirred at room temperature for 2 h. After evaporating the solvent to dryness and washing with pentane a white solid is obtained. White crystals of **5** are obtained after recrystallization with 1,2-dichloroethane and pentane (1 : 10). Yield: 49%. Anal. calcd. for $C_{26}H_{14}F_{10}N_4OPd{\cdot}CH_2Cl_2$ (694.82): C, 41.59; H, 2.07; N, 7.18; found: C, 41.03; H, 2.36; N, 6.94. IR (KBr, cm^{-1}): 785 (C_6F_5).

Pd(C_6F_5)$_2$(bpzmArOH), 6. The method is similar to that used for complex **5**. Amounts are as follows: 100 mg (0.18 mmol) of Pd(C_6F_5)$_2$(cod) and 43 mg (0.18 mmol) of bpzmArOH. **6** is obtained as a white solid. Yield: 66% . Anal. calcd. for $C_{25}H_{12}F_{10}N_4OPd{\cdot}0.5Et_2O$ (730.78): C, 45.17; H, 2.38; N, 7.80; found: C, 45.68; H, 2.29; N, 8.09. IR (KBr, cm^{-1}): 795 (C_6F_5).

Pd(C_6F_5)$_2$(bpz*mArOMe), 7. The method is similar to that used for complex **5**. Amounts are as follows: 40 mg (0.07 mmol) of Pd(C_6F_5)$_2$(cod) and 20 mg (0.07 mmol) of bpz*mArOMe. White crystals of **7** are obtained. Yield: 53%. Anal. calcd. for $C_{30}H_{22}F_{10}N_4OPd{\cdot}0.5C_2H_4Cl_2$ (800.41): C, 46.52; H, 3.02; N, 6.99; found: C, 46.23; H, 2.55; N, 7.57. IR (KBr, cm^{-1}):790 (C_6F_5).

Pd(C_6F_5)$_2$(bpz*mArOH), 8. The method is similar to that used for complex **5**. Amounts are as follows: 60 mg (0.11 mmol) of Pd(C_6F_5)$_2$(cod) and 30 mg (0.12 mmol) of bpz*mArOH. A white solid of **8** is obtained. Yield: 78%. Anal. calcd. for $C_{29}H_{20}F_{10}N_4OPd$ (736.90): C, 47.27; H, 2.74; N, 7.60; found: C, 47.10; H, 2.97; N, 7.15. IR (KBr, cm^{-1}): 780 (C_6F_5).

Pd(C_6F_5)$_2$(bpz*mCy), 9. The method is similar to that used for complex **5**. Amounts are as follows: 52 mg (0.18 mmol) of **3** and 100 mg (0.18 mmol) of Pd(C_6F_5)$_2$(cod) in 10 mL of acetone. After evaporating the solvent to dryness the residue is recrystallized from 1,2-dichloroethane–pentane (1 : 10). White crystals of **9** are obtained. Yield: 86%. Anal. calcd. for $C_{29}H_{26}F_{10}N_4Pd$ (726.94): C, 47.92; H, 3.61; N, 7.61; found: C, 48.01; H, 3.82; N, 7.63. IR (KBr, cm^{-1}): 781 (C_6F_5).

Pd(C_6F_5)$_2$(bpz*mFec), 10. The method is similar to that used for complex **9**. Amounts are as follows: 80 mg (0.21 mmol) of **4** and 113 mg (0.21 mmol) of Pd(C_6F_5)$_2$(cod) in 15 mL of acetone. Orange crystals of **10** are obtained. Yield: 72%. Anal. calcd. for $C_{33}H_{24}F_{10}FeN_4Pd$ (828.82): C, 47.82; H, 2.92; N, 6.76; found: C, 47.77; H, 2.91; N, 6.63. IR (KBr, cm^{-1}): 781 (C_6F_5).

Pd(C_6F_5)$_2$(pzpy), 11. Pd(C_6F_5)$_2$(cod) (105 mg, 0.19 mmol) and 28 mg (0.192 mmol) de pzpy are mixed in 10 mL of THF. After stirring at reflux for 24 h, the solution is evaporated to dryness and the white solid washed with diethyl ether. Yield: 85%. Anal. calcd. for $C_{20}H_7F_{10}N_3Pd$ (585.71): C, 41.74; H, 1.58; N, 6.95; found: C, 41.78; H, 1.28; N, 6.74. IR (Nujol, cm^{-1}): 796, 774 (C_6F_5).

Pd(C_6F_5)$_2$(pzpm), 12. The method is similar to that used for complex **11**. Amounts are as follows: 200 mg (0.36 mmol) of Pd(C_6F_5)$_2$(cod) and 53 mg (0.36 mmol) of pzpm. A pale yellow solid is obtained. Yield: 85%. Anal. calcd. for $C_{19}H_6F_{10}N_4Pd$ (586.69): C, 40.38; H, 1.77; N, 8.97; found: C, 40.05; H, 1.37; N, 8.77. IR (Nujol, cm^{-1}): 786, 774 (C_6F_5).

Pt(C_6F_5)$_2$(pzpm), 13. Pt(C_6F_5)$_2$(THF)$_2$ (60 mg, 0.09 mmol) and 13 mg (0.09 mmol) of pzpm are dissolved in 10 mL of CH_2Cl_2 and the solution is stirred for 2 h at room temperature. The solution is evaporated to dryness and a white solid of **13** is obtained. Yield: 83%. Anal. calcd. for $C_{19}H_6F_{10}N_4Pt$ (674.37): C, 33.79; H, 0.89; N, 8.30; found: C, 34.06; H, 1.02; N, 8.10. IR (Nujol, cm^{-1}): 800, 772 (C_6F_5).

Pd(C_6HF_4)$_2$(pzpm), 14. Pd(C_6HF_4)$_2$(cod) (100 mg, 0.19 mmol) and 28.6 mg (0.19 mmol) of pzpm are dissolved in 10 mL of tetrahydrofurane. The solution is stirred for 48 h. The solution is evaporated to dryness, the residue is washed with pentane and a white solid of **14** is obtained. Yield: 65%. Anal. calcd. for $C_{19}H_8F_8N_4Pd$ (550.71): C, 39.25; H, 1.46; N, 10.17; found: C, 38.88; H, 1.50; N, 9.94. IR (Nujol, cm^{-1}): 826, 782 (C_6F_5).

Structure determination of 10

Suitable crystals of **10** were grown from toluene–pentane (1 : 10). A white crystal of approximate dimensions $0.4 \times 0.3 \times 0.2$ mm^3 was mounted in a glass capillary. Intensity data were collected at 298 K on a Nonius-Mach3 diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71070$ Å) using the $\omega/2\theta$ scan technique to a maximum value of 56°. The intensities of two representative reflections measured every hour did not change significantly during the course of the data collection. The crystal is monoclinic, of space group $P2_1/n$, with one molecule of **10** per asymmetric unit. Data were corrected in the usual fashion for Lorentz and polarization effects and empirical absorption correction was not necessary ($\mu = 11.22$ cm^{-1}). The structure was solved using direct methods (SIR92).[42] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL97).[43] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and were refined isotropically.

CCDC reference number 168151. See http://www.rsc.org/suppdata/nj/b1/b108139j/ for crystallographic data in CIF or other electronic format.

Acknowledgements

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