Can a single C–H⋯F–C hydrogen bond make a difference? Assessing the H⋯F bond strength from 2-D ^{1}H-^{19}F CP/MAS NMR†

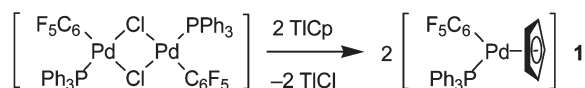Gerhard Althoff,[a] José Ruiz,*[b] Venancio Rodríguez,[b] Gregorio López,[b] José Pérez[c] and Christoph Janiak*[d]

Contrary to common belief a single C–H⋯F–C contact in $[(\eta^5\text{-}C_5H_5)Pd(C_6F_5)(PPh_3)]$ is strong enough to pair two independent molecules and render them crystallographically different as suggested by its strongest ^{1}H–^{19}F dipole–dipole coupling in a 2-D CP/MAS PILGRIM NMR experiment together with solid state 1-D ^{19}F{^{1}H} and 2-D ^{19}F RFDR NMR spectroscopy – thereby proving the power of 2-D solid-state NMR for assessing the strength of supramolecular contacts.

Organometallic complexes of palladium containing cyclopentadienyl (Cp) ligands coordinated to the metal in a η^5-fashion are rare.[1,2] Consequently, the chemistry of η^5-CpPd is not as developed as that of earlier transition metals. We have found that the complex $[(\eta^5\text{-}Cp)Pd(C_6F_5)(PPh_3)]$ **1** can be easily prepared in excellent yields by reacting the chloro-bridging organopalladium dimer $[\{(Pd(C_6F_5)(PPh_3)\}_2(\mu\text{-}Cl)_2]$ with cyclopentadienylthallium:

$$
\begin{bmatrix} F_5C_6 & Cl & PPh_3 \\ & Pd \quad Pd & \\ Ph_3P & Cl & C_6F_5 \end{bmatrix} \xrightarrow[-2\ TlCl]{2\ TlCp} 2\begin{bmatrix} F_5C_6 \\ Pd\!-\!\text{(Cp)} \\ Ph_3P \end{bmatrix}\ \mathbf{1}
$$

The complex is air-stable, both in the solid state and in solution. The new complex has been characterized by partial elemental analyses and spectroscopic (IR and ^{1}H, ^{19}F, ^{13}C and ^{31}P NMR) methods. The ^{19}F NMR spectrum in solution of complex **1** reveals the presence of a freely rotating pentafluorophenyl ring which gives three resonances (in the ratio 2 : 2 : 1) for the o-, m-, and p-fluorine atoms.

Red crystals suitable for X-ray diffraction studies were obtained by slow diffusion of hexane into a dichloromethane solution of **1**. Crystallographic data sets were collected at 100 and 293 K.‡ The structural features for both the low and room temperature structure are the same and do not necessitate a distinction in the following discussion. Fig. 1 shows the asymmetric unit in the

structure of **1** which contains two independent molecules, hereafter termed Pd1 and Pd2.

In both Pd1 and Pd2 the Pd−C(Cp) trans to the σ-pentafluorophenyl ligand is the shortest. A similar pattern has already been observed in a number of other structures of nickel, palladium and platinum cyclopentadienyl complexes.[3] Such M–(Cp) (M = Ni, Pd, Pt) bond length differences have been rationalized in terms of the trans influence of the σ-aryl ligand. Also the variation in C–C bond lengths in the Cp rings of **1** is similar to other cyclopentadienyl complexes of nickel, platinum and especially palladium[3] and could again be attributed to the different trans influence of the σ-C_6F_5 and PPh_3 ligands. The Pd–C_6F_5 bond lengths are in the range found in the literature for pentafluorophenyl–palladium complexes.[4] The solid-state structure of **1** exhibits two very similar independent molecules in the asymmetric unit (Pd1 and Pd2). A comparison of the orthogonal coordinates of both molecules, a comparison of the bonds of the molecules, and a comparison of the bond angles of the molecules reveals a high degree of conformational similarity and shows no clearly discernable conformational difference which would explain their crystallographic differentiation. As a visual presentation of their similarity Fig. 2 shows an overlay of the two independent molecules.
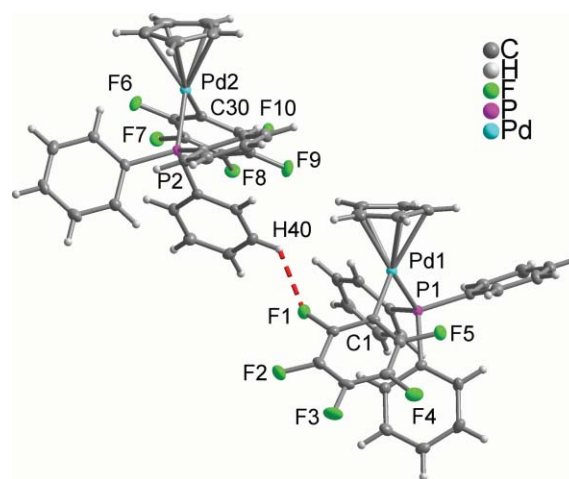
Fig. 1 Asymmetric unit with the two independent molecules of **1**, showing the short C–H⋯F–C bond. Selected distances (Å) and angles (°) (at 100 K): Pd–C(Cp) 2.273(2)–2.375 Å, Pd–Ct(Cp) 1.9929(12)/1.9900(13), Pd–C(Ph) 2.026(2)/2.021(2), Pd–P 2.2306(6)/2.2406(6), C–C(Cp) 1.380(5)–1.458(4), C(Ph)–Pd–P 93.23(7)/92.14(7), Ct(Cp)–Pd–P 134.99(4)/137.10(4), Ct(Cp)–Pd–C(Ph) 131.64(8)/130.74(8) for Pd1/Pd2, respectively. A full and comparative listing with the 293 K structure can be found in the ESI.†

[a] Bruker Biospin GmbH, Silberstreifen, 76287, Rheinstetten, Germany
[b] Departamento de Química Inorgánica, Universidad de Murcia, 30071, Murcia, Spain. E-mail: jruiz@um.es
[c] Departamento de Ingeniería Minera, Geológica y Cartográfica. Área de Química Inorgánica, Universidad Politécnica de Cartagena, E-30203, Cartagena, Spain
[d] Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, 79104, Freiburg, Germany. E-mail: janiak@uni-freiburg.de

Fig. 2 Overlay of the molecular structures of Pd1 (in gray) and Pd2 (in black) in **1** by specifying the atoms of the P–Pd–C(ipso-aryl)-moiety as three pairs in the two structures (rms = 0.0131).

The existence of these two crystallographically different molecules in the asymmetric unit is independent of temperature between +20 °C (293 K) and −173 °C (100 K), that is, the space group does not change in this temperature regime. The explanation must obviously be sought in the intermolecular interactions. There is apparently a non-covalent, supramolecular interaction which is sufficiently different between a pair of the independent molecules from the remainder of the intermolecular contacts, such that two similar conformers are rendered crystallographically different. Obvious intermolecular interactions are π–π and C–H···π contacts[5–7] and C–H···F–C hydrogen bonds.[8,9] Despite the π-systems in **1** no strong intermolecular π–π or differentiating C–H···π interactions can be found (analysis in ESI).†

Each C_6F_5-ring in Pd1 and Pd2 is surrounded by C–H moieties from phenyl or cyclopentadienyl rings, that is, the intermolecular packing bristles with C–H···F–C contacts (Fig. 3). There are C–H···F–C hydrogen bonds between symmetry related molecules of Pd1, between symmetry related molecules of Pd2 and between
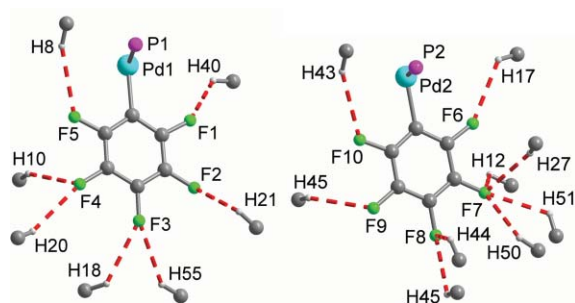
**Fig. 3** C–H···F–C hydrogen bonds to the C_6F_5 ring on Pd1 and Pd2. H···F distances (Å): Pd1: H40···F1 2.39, H10···F4 2.58, H20···F4 2.60, H18···F3 2.74, H21···F2 2.79, H8···F5 2.79, H55···F3 2.87, Pd2: H44···F8 2.50, H51···F7 2.60, H27···F7 2.63, H17···F6 2.65, H45···F8 2.67, H12···F7 2.75, H45···F9 2.78, H50···F7 2.85, H43···F10 2.86 (100 K structure, cutoff H···F < 2.88 Å, symmetry relations can be found in Table 3 of the ESI).†

Pd1–Pd2 of different symmetry relations. While this does not seem encouraging for the required differentiation, there is one C–H···F–C contact that stands out from all the others because of its close H···F distance: It is the contact between C40–H40 (on Pd2) and F1–C1(*ortho*) (on Pd1) with an H···F distance of only 2.39 or 2.42 Å with a C–H···F angle of 132 or 136° at 100 or 293 K, respectively (Fig. 1). The next nearest H···F contacts start at 2.50 or 2.58 Å, respectively (between symmetry related molecules of Pd2). H···F contacts around or below 2.40 Å in C–H···F–C hydrogen bonds are still among the shortest contacts found in such interactions.[8] Therefore, we view this (Pd2)C40–H40···F1–C(*ortho*)(Pd1) contact as special. There is only one such short contact in the structure of compound **1** and it is also a contact which exists only within a pair of Pd1–Pd2 molecular units. Also, this contact varies least in distance upon temperature variation when compared to the other intermolecular C–H···F–C contacts (see column Δ(H···F)₁₀₀₋₂₉₃ in Table 3 of ESI).† In a structural study on Pt(C_6F_5)₂-naphthyridine derivatives Forniés *et al.* concluded a prevalence of C–H···F–C hydrogen bonds over π–π interactions in their supramolecular aggregation,[10] while Dunitz and Taylor stated that "organic fluorine (C–F) hardly ever accepts hydrogen bonds",[11] and Hulliger *et al.* conclude that "the role of fluorine in crystal engineering is not yet clear". Except for phenyl-perfluorphenyl π-stacking, other observed fluorine interactions are generally weak.[8]

The above interpretation based on single crystal X-ray structures relies on a high quality data set, a correct space group assignment and the (often, but not always correct) bond strength–bond length relationship. For an independent investigation of the H···F contacts in **1** we applied ¹⁹F{¹H} solid state MAS NMR spectroscopy. A 1-D ¹⁹F-CP-MAS spectrum in Fig. 4 shows 9 signals in two sets of peaks. Direct excitation spectra (data not shown) yield an integral ratio of 2 : 3. This agrees with the four (crystallographically) non-equivalent *ortho*-F in **1** (2 for Pd1 and Pd2 each) and the six different *meta*- and *para*-F from which five
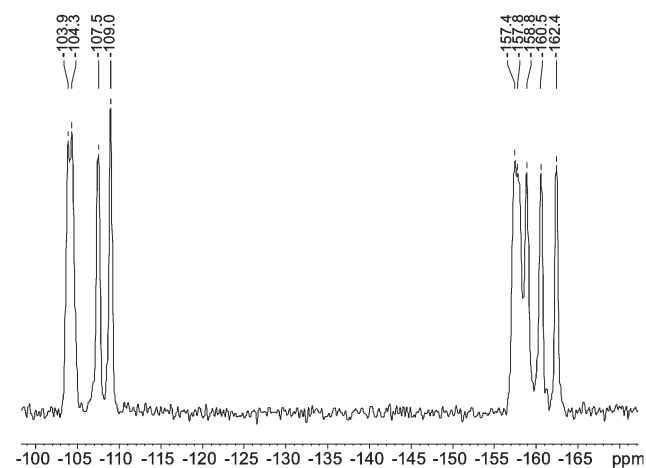
Fig. 4 Room temperature 1-D ¹⁹F-CP/MAS spectrum at 33.33 kHz spinning speed acquired on a Bruker AV500 spectrometer operating at a ¹⁹F frequency of 470.5 MHz. A 2.5 mm MAS rotor was used, the contact time was set to 500 μs at 90 kHz ¹⁹F RF, 90 kHz of proton decoupling was applied during acquisition using the SPINAL64 scheme. 8 scans were acquired at 10 s recycle delay. ¹⁹F chemical shifts were calibrated using external hexafluorobenzene (−163 ppm).
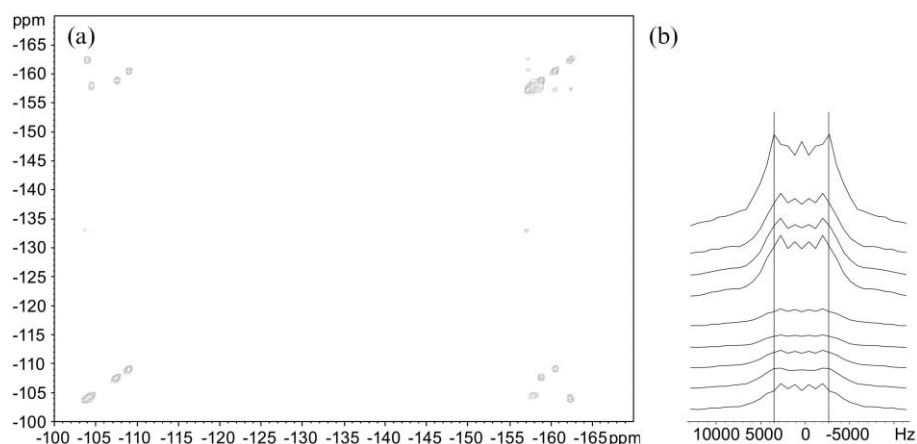
Fig. 5 (a) Room temperature ^{19}F RFDR (radio frequency driven dipolar recoupling) spectrum at 33.33 kHz spinning. The mixing time was set to 32 rotor periods, the contact time was 500 μs, 90 kHz proton decoupling was applied. (b) Results from the PILGRIM experiment showing top to bottom the leftmost to rightmost peak from the 2-D ^1H-^{19}F-spectrum. The data were acquired at room temperature on a Bruker AV400 spectrometer operating at a ^{19}F frequency of 376.4 MHz. A 4 mm rotor was used spinning at 15 kHz. In the indirect dimension (F1) 80 points were acquired by incrementing the Lee Goldburg cross polarisation in steps of 10 μs resulting in a spectral width of 100 kHz in F1. Proton decoupling was applied at an RF field strength of 80 kHz employing the SPINAL64 scheme.

could be resolved. Further assignment of the NMR signals and further proof of the existence of two non-equivalent C_6F_5-groups is achieved by 2-D ^{19}F RFDR (radio frequency driven dipolar recoupling) measurements. This technique correlates dipolarly (through space) coupled ^{19}F sites. Usually, only cross peaks for nearest neighbors will show up. The existence of a cross peak reveals that the corresponding two sites are in the same C_6F_5-group. The spectrum shown in Fig. 5a exhibits two distinct cross peak networks belonging to the two non-equivalent C_6F_5-groups (tentative assignment in ESI).† To assess the strength of the ^1H–^{19}F dipole–dipole coupling the PILGRIM experiment was used.[12] This procedure measures the dipole spectrum in the indirect dimension of the 2-D experiment. The width of the spectrum, that is, the distance between the singularities is a measure of the coupling strength. Fig. 5b displays (top to bottom for the leftmost to rightmost peak of Fig. 4) the columns for the nine differentiated fluorine positions taken from the 2-D spectrum. The maximum coupling (uppermost spectrum) belongs to the set of the four *ortho*-F. The PILGRIM spectrum does not identify the second strongest coupling expected for *para*-F8 due to low resolution (the RFDR result indicates that the F8 peak is not resolved). Yet, the finding agrees with a short H40···*ortho*-F1 contact of 2.39/2.42 Å and a second-shortest H44···*para*-F8 contact of 2.50/2.58 Å with the next-nearest H···F contacts being 2.58/2.67 Å (100 K/293 K structure, respectively).

In summary, we could show that C–H···F–C contacts or even a single C–H···F–C contact are strong enough to pair two molecules and render them crystallographically different in the solid state. This is counter-intuitive to the common current belief that hydrogen bonds involving organic fluorine are generally weak. Compound **1** adds a positive example to the role of fluorine in crystal engineering.[13]

Notes and references

1 V. V. Grushin, C. Bensimon and H. Alper, *Organometallics*, 1993, **12**, 2737.
2 G. K. Anderson, R. J. Cross, L. Manojiovic-Muir and K. W. Muir, *Organometallics*, 1988, **7**, 1520.
3 G. K. Anderson, R. J. Cross, K. W. Muir and L. Manojilovic-Muir, *J. Organomet. Chem.*, 1989, **362**, 225 and references therein.
4 J. Forniés, F. Martínez, R. Navarro and E. P. Urriolabeitia, *J. Organomet. Chem.*, 1995, **495**, 185; J. Ruiz, M. T. Martínez, F. Florenciano, V. Rodríguez, G. López, J. Pérez, P. A. Chaloner and P. B. Hitchcock, *Inorg. Chem.*, 2003, **42**, 3650; J. Ruiz, M. T. Martínez, F. Florenciano, V. Rodríguez, G. López, J. Pérez, P. A. Chaloner and P. B. Hitchcock, *Dalton Trans.*, 2004, 929.
5 C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.
6 M. Nishio, *CrystEngComm*, 2004, **6**, 130; M. Nishio, M. Hirota and Y. Umezawa, *The CH/π interaction (evidence, nature and consequences)*, Wiley-VCH, New York, 1998; Y. Umezawa, S. Tsuboyama, K. Honda, J. Uzawa and M. Nishio, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1207;

C. Janiak, S. Temizdemir, S. Dechert, W. Deck, F. Girgsdies, J. Heinze, M. J. Kolm, T. G. Scharmann and O. M. Zipffel, *Eur. J. Inorg. Chem.*, 2000, 1229.

7 T. Dorn, A.-C. Chamayou and C. Janiak, *New J. Chem.*, 2006, **30**, 156.

8 K. Reichenbächer, H. I. Süss and J. Hulliger, *Chem. Soc. Rev.*, 2005, **34**, 22.

9 G. R. Desiraju and T. Steiner, The Weak Hydrogen Bond, *IUCr Monographs on Crystallography*, Oxford University Press, 1999, vol. 9, pp. 205–213 and references therein.

10 J. M. Casas, B. E. Diosdado, L. R. Falvello, J. Forniés, A. Martin and A. J. Rueda, *Dalton Trans.*, 2004, 2733.

11 J. D. Dunitz and R. Taylor, *Chem. Eur. J.*, 1997, **3**, 89.

12 M. Hong, X. Yao, K. Jakes and D. Huster, *J. Phys. Chem. B*, 2002, **106**, 7355.

13 S. Takahashi, T. Jukurogi, T. Katagiri and K. Uneyama, *CrystEngComm*, 2006, **8**, 320; A. R. Choudhury and T. N. Guru Row, *CrystEngComm*, 2006, **8**, 265; R. Mariaca, N.-R. Behrnd, P. Eggli, H. Stoeckli-Evans and J. Hulliger, *CrystEngComm*, 2006, **8**, 222; D. G. Golovanov, K. A. Lyssenko, M. Yu. Antipin, Y. S. Vygodskii, E. I. Lozinskaya and A. S. Shaplov, *CrystEngComm*, 2005, **7**, 53; A. Schwarzer, W. Seichter, E. Weber, H. Stoeckli-Evans, M. Losada and J. Hulliger, *CrystEngComm*, 2004, **6**, 567; G. R. Desiraju, *Acc. Chem. Res.*, 2002, **35**, 565; V. R. Vangala, A. Nangia and V. M. Lynch, *Chem. Commun.*, 2002, 1304.