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Cyclopalladated acetate dimers: Crystal structures and VT-NMR

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Abstract

The X-ray structure of two cyclopalladated acetate bridged dimers has been solved, and they are shown to exhibit an open-book type core, analogous to those that have been previously reported. Variable temperature NMR studies on these molecules demonstrates that this core persists in chloroform solution, resulting in restrictions to the movement of ancillary parts of the molecule. The barrier to rotation of a pendant phenyl ring against this core has been measured: $\Delta H^{\ddagger} = 56$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 0$.

Keywords: Cyclometallation; Cyclopalladation; Palladium; VT-NMR; X-ray structure

1. Introduction

The study of the cyclometallation reaction is of considerable interest, both from a mechanistic point of view [1] and because of its role in the functionalisation of C–H bonds [2–6]. We have recently published a couple of papers dealing with the mono- and di-cycloplatination of diphenylpyridines [7,8], and another one that dealt with the unusual situation that can lead to the formation of a carbene species [9]. Here, we discuss some aspects of the cyclopalladation of diphenylpyridines, and the structure of the resulting complexes. The cyclopalladation reaction is of particular interest due to the role of palladium catalysts in C–C bond forming reactions [10], with a recent computational study identifying likely agostic intermediates in the reaction pathway [11].

2. Synthesis

Two new organopalladium compounds have been synthesized, via the direct reaction of a substituted pyridine with palladium acetate which proceeds cleanly at 60 °C in acetic acid to yield a cyclopalladated species in high yield (Scheme 1). A cursory inspection of the NMR spectra reveals nothing more unusual than overlapping peaks and further purification is not found to be necessary: crystals of a suitable standard for single-crystal X-ray diffraction could be isolated easily. A crystal of pure diphenyl pyridine was also the subject of an X-ray diffraction study; nothing unusual was revealed, but details are recorded here for completeness (Fig. 1).

3. Solid-state structures

The crystal structures of both (**1**) and (**2**) were solved. Whilst crystals of (**1**) were twinned and the structure could not be refined to publication standard, it is clear that it has the same principal features exhibited by the structure of (**2**) (Fig. 2), which we will discuss in more detail: selected bond lengths and angles are recorded in Table 1. Both (**1**) and (**2**) exhibit dimeric structures with the two halves related by a C_2 rotation. At the heart of the molecules are the two palladiums bridged by the two acetates; these bridges fold the two halves of the molecule back on each other, rather like an open book. In the two structures reported here we have a close Pd–Pd

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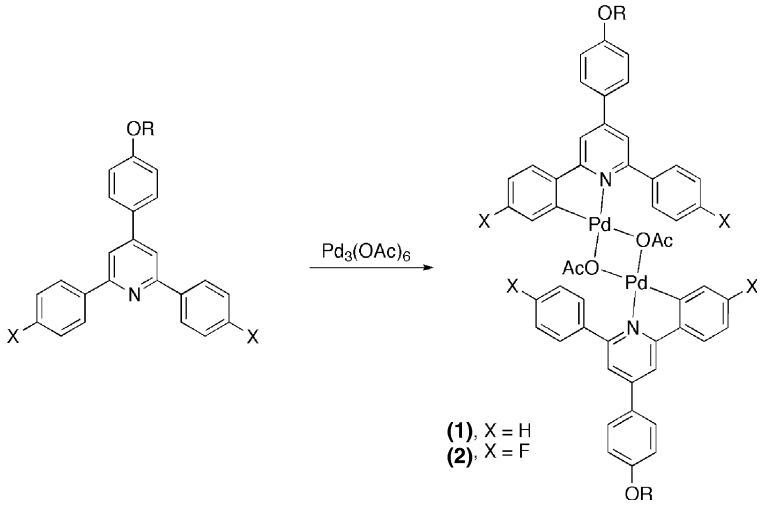

Scheme 1.

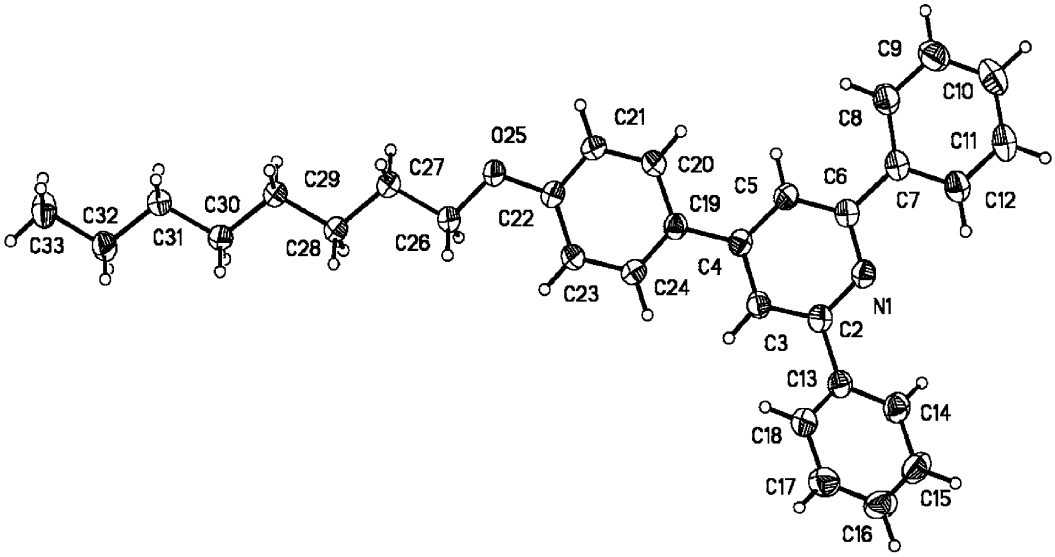

Fig. 1. The X-ray structure of the diphenyl pyridine ligand.

contact of 2.9029(12) Å in (**1**) and 2.9067(9) Å in (**2**); the planes of the cyclometallated rings end up being close to parallel (inclined at 11.6(6) and11.8(3)° to each other in (**1**) and (**2**), respectively), and the unmetallated phenyl rings are inclined at angles of 59.4(3) and 43.9(3)° to the pyridine ring. In the structure of (2) the Pd–N distance is 2.074(5) Å, the Pd–C distance is 1.969(6) Å. This Pd–C distance is significantly shorter that the average Pd–C single bond, in line with the expectation that the five membered metallocycle has significant aromatic character [12]; other authors [13] have related short Pd–C bond distances with the π back bonding of the metallic centre to the aromatic system. The Pd–O distances are 2.159(5) (O *trans* to C) and 2.058(5) (O *trans* to N), with this difference being readily attributed to the greater *trans* influence shown by carbon, compared with nitrogen.

A survey of the Cambridge Crystallographic Database [14] reveals 78 similar structures of dimeric cyclopalladated compounds with a carboxyl bridged core. The mean Pd–Pd distance in these structures is 2.952 Å, with max and min values at 2.823 and 3.281 Å (one outlier with a Pd–Pd distance of 3.413 Å is reported for the hugely sterically crowded cyclopalladated di(orthotolyl)(*t*-butyl)phosphine compound [15]). The question of when a Pd–Pd interaction constitutes a bond seems clear: the covalent radius of a square planar palladium is reported as being 1.31 Å [16], thus only with complexes having Pd–Pd distances of 2.62 Å or less does the question arise. All of the 78 structures mentioned above have Pd–Pd distances greater than 2.62 Å and thus none should be considered as having a Pd–Pd bond. Interestingly, of these 78 structures, 14 (mean Pd–Pd distance = 2.872, min = 2.831, max = 2.939 Å) are shown as having a bond, whereas 64 (mean Pd–Pd distance = 2.969, min = 2.823, max = 3.281 Å) are shown as not having a bond. Our Pd–Pd distance is thus well within the normal range.

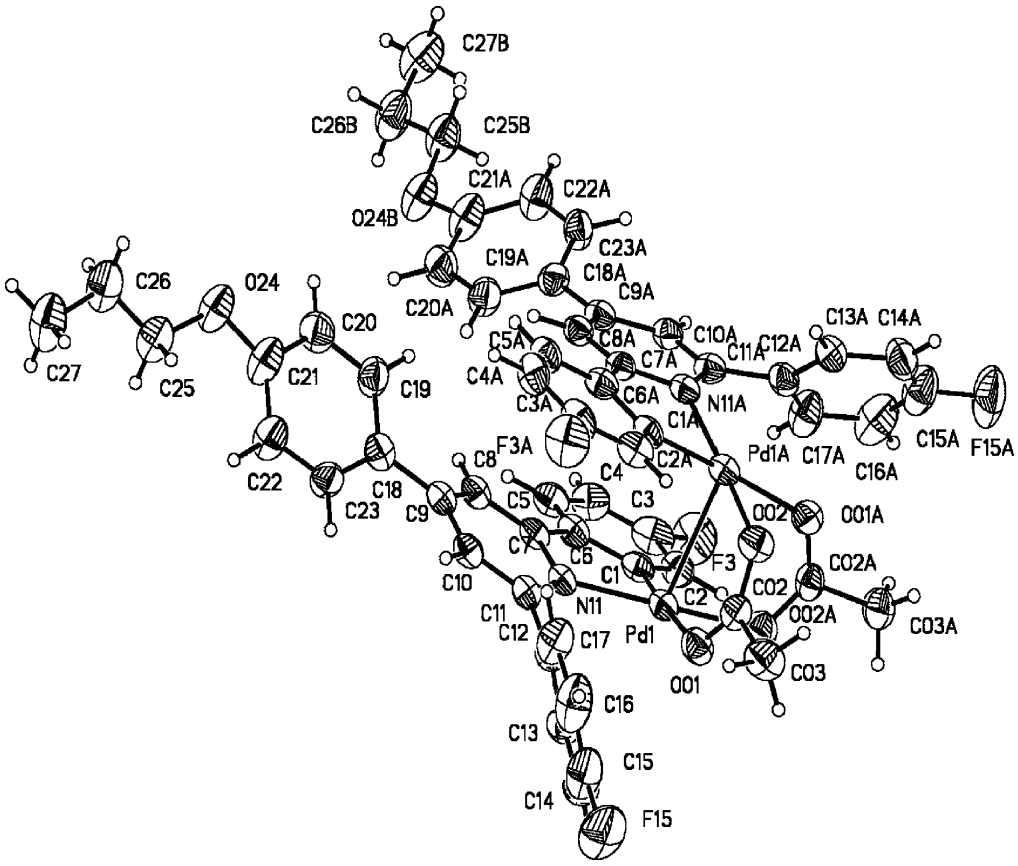

Fig. 2. The X-ray structure of compound (**2**).

4. Variable temperature NMR

A more detailed look at the solution ^{1}H NMR data on compounds (**1**) and (**2**) shows that some of the protons on the non-palladated ring are so broad as to be lost in the baseline at ambient temperature. A more in depth study of these spectra was thus undertaken. Similar results were obtained for both (**1**) and (**2**), but the less crowded nature of the ^{1}H spectrum of (**2**) made it more amenable to study.

Fig. 3 shows a stacked plot of some of the variable temperature ^{1}H NMR spectra of compound (**2**), in chloroform solution, in the aromatic region of the spectrum; Fig. 4 shows the labelling system we have used. Only the signals relating to the protons W, X, Y and Z change significantly with temperature, and it is worth noting that we can unambiguously distinguish protons W and X from Y and Z from the coupling to the ^{19}F on the ring. At 333 K the signals for protons W and X are a broad hump, but clearly identifiable at around 7.5 ppm; as the temperature is decreased this signal gets broader (and disappears into the baseline at about room temperature) before separating out into two clear signals at 7.84 and 7.20 ppm. We measured the separation of these two peaks to be 323 Hz (on a 500 MHz spectrometer) with a coalescence temperature of 293 K. The signal for protons Y and Z are already at a high temperature limit at room temperature, but separate into the two signals at 7.14 and 7.07 ppm on cooling. We measured the separation of these two peaks to be 32 Hz (on a 500 MHz spectrometer) with a coalescence temperature of 268 K. The only plausible reason for the signal for proton W being different from that of proton X (and for that of Y being different to that of Z) is that the unmetallated phenyl ring cannot rotate freely with respect to the pyridine ring (on the NMR timescale) and that the two sides of the pyridine ring are somehow different. These conditions can only be met if the acetate bridges, together with the open book shape of the core, persist in solution. Thus, we regard our results as proof of exactly that: the cyclopalladated carboxyl bridged dimers that are known to exist in the solid state maintain their structure in chloroform solution.

It is apparent that the two peaks for W and X are significantly different in the ^{1}H NMR, and an inspection of the X-ray structure suggests why: one of the hydrogens W and X points directly at a fluorine in the other half of the dimer, whereas the other one points into free space. Similarly the two protons Y and Z are clearly pointing in different directions, but both are largely pointing into free space, and this results in the relatively small difference in their chemical shifts.

We can use the coalesence temperatures observed to extract values for the barrier to interconversion of the two sets of signals, using standard techniques. The $\Delta G^{\ddagger}$

Table 1
Bond lengths (Å) and angles (°) for (**1**)

Pd(1)–C(1)	1.969(6)
Pd(1)–O(02)#1	2.058(5)
Pd(1)–N(11)	2.074(5)
Pd(1)–O(01)	2.159(5)
Pd(1)–Pd(1)#1	2.9067(9)
C(1)–C(6)	1.413(10)
C(1)–C(2)	1.414(9)
C(2)–C(3)	1.361(11)
C(3)–C(4)	1.362(11)
C(3)–F(3)	1.379(8)
C(4)–C(5)	1.359(10)
C(5)–C(6)	1.380(9)
C(6)–C(7)	1.488(9)
C(7)–N(11)	1.366(8)
C(7)–C(8)	1.380(9)
C(8)–C(9)	1.406(9)
C(9)–C(10)	1.395(9)
C(9)–C(18)	1.485(10)
C(10)–C(11)	1.379(9)
N(11)–C(11)	1.366(7)
C(11)–C(12)	1.479(9)
F(15)–C(15)	1.384(10)
C(1)–Pd(1)–O(02)#1	92.0(2)
C(1)–Pd(1)–N(11)	81.1(2)
O(02)#1–Pd(1)–N(11)	172.9(2)
C(1)–Pd(1)–O(01)	176.9(2)
O(02)#1–Pd(1)–O(01)	85.1(2)
N(11)–Pd(1)–O(01)	101.8(2)
C(6)–C(1)–C(2)	117.6(6)
C(6)–C(1)–Pd(1)	115.4(5)
C(2)–C(1)–Pd(1)	127.0(6)
C(3)–C(2)–C(1)	118.6(7)
C(2)–C(3)–C(4)	123.6(7)
C(5)–C(6)–C(1)	120.5(6)
C(5)–C(6)–C(7)	125.7(7)
C(1)–C(6)–C(7)	113.7(6)
N(11)–C(7)–C(8)	121.7(6)
N(11)–C(7)–C(6)	114.4(6)
C(8)–C(7)–C(6)	123.9(6)
C(7)–N(11)–C(11)	118.6(5)
C(7)–N(11)–Pd(1)	112.5(4)
C(11)–N(11)–Pd(1)	127.8(4)

at 293 K can be calculated as 55.78 kJ mol^{-1} and at 268 to be 55.99 kJ mol^{-1}. Given likely uncertainty in the measurement of the coalescence temperatures (±2 K) and peak separation (±5 Hz) our estimate of the uncertainty in the $\Delta G^{\ddagger}$ values is 0.9 kJ mol^{-1}. This leads us to conclude that the Gibbs energy of activation is the same at both temperatures, and thus that (to the accuracy of our measurements) the $\Delta H^{\ddagger}$ is 56 kJ mol^{-1}, and the entropy of activation ($\Delta S^{\ddagger}$) is zero. An entropy of activation that is zero is consistent with an intramolecular process that does not disrupt solvent–solute interactions.

The enthalpy of activation we measure is very similar to the barrier to rotation about the C–N bond in isonicitinamide [17], which has been measured as 59.2 kJ mol^{-1}, and is in between the 91.6 kJ mol^{-1} reported for a trisubstituted biphenyl [18] and the 31.5 kJ mol^{-1} reported for 2,2′-bipyridine [18]. We propose that the barrier we have observed represents the barrier to rotation of the unmetallated phenyl ring against the pyridine ring. We would expect this barrier to be greater than that that exists in 2,2′-bipyridine (and that of the other, alkoxy substituted, ring which does not show any additional complications in the NMR at the temperatures we used) as the palladium acetate bridged core provides additional steric constraints. We would expect this barrier to be less than that that exists for a trisubstituted biphenyl. The zero entropy of activation is also consistent with this intramolecular process. We do not feel we need to invoke any additional agostic type interaction of hydrogens W and X with the palladium centre to account for the size of the barrier.

5. Conclusions

The structure of cyclopalladated acetate bridged dimers is known to exhibit an open-book type core in the solid state. This core has been shown to persist in chloroform solution, resulting in restrictions to the movement of ancillary parts of the molecule. We believe the size of the barrier can be accounted for solely on the basis of a steric interaction.

6. Experimental

6.1. General

All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on a Bruker Avance 500 in $CDCl_3$ and are referenced to external TMS, assignments being made with the use of decoupling, nOe and the DEPT and COSY pulse sequences. All elemental analyses were performed by Warwick Analytical Service.

7. Pyridine ligands

The 2,4,6-trisubstituted pyridines were synthesized via the Kröhnke route [19] or its solventless adaptation [20]. Crystals of 4-(4-octyloxy-phenyl)-2,6-diphenylpyridine suitable for X-ray structure determination were grown from a chloroform solution, and the structural data are included as supporting information.

7.1. Cyclopalladated dimer (*1*)

4-(4-Octyloxy-phenyl)-2,6-diphenyl)-pyridine (0.116 g, 2.67×10^{-4} mol) and palladium acetate (0.060 g, 2.67×10^{-4} mol) were suspended in acetic acid (80 ml) and heated (70 °C, 48 h). The acetic acid was then removed under vacuum, and the remaining yellow solid dissolved in dichloromethane filtered to remove traces of palladium black. The solvent was removed to give the product (0.223 g, 1.86×10^{-4} mol, 70%). A single crystal suitable for X-ray diffraction was grown by diffusing diethyl ether into a chloroform solution: the structural data are included as supporting information.

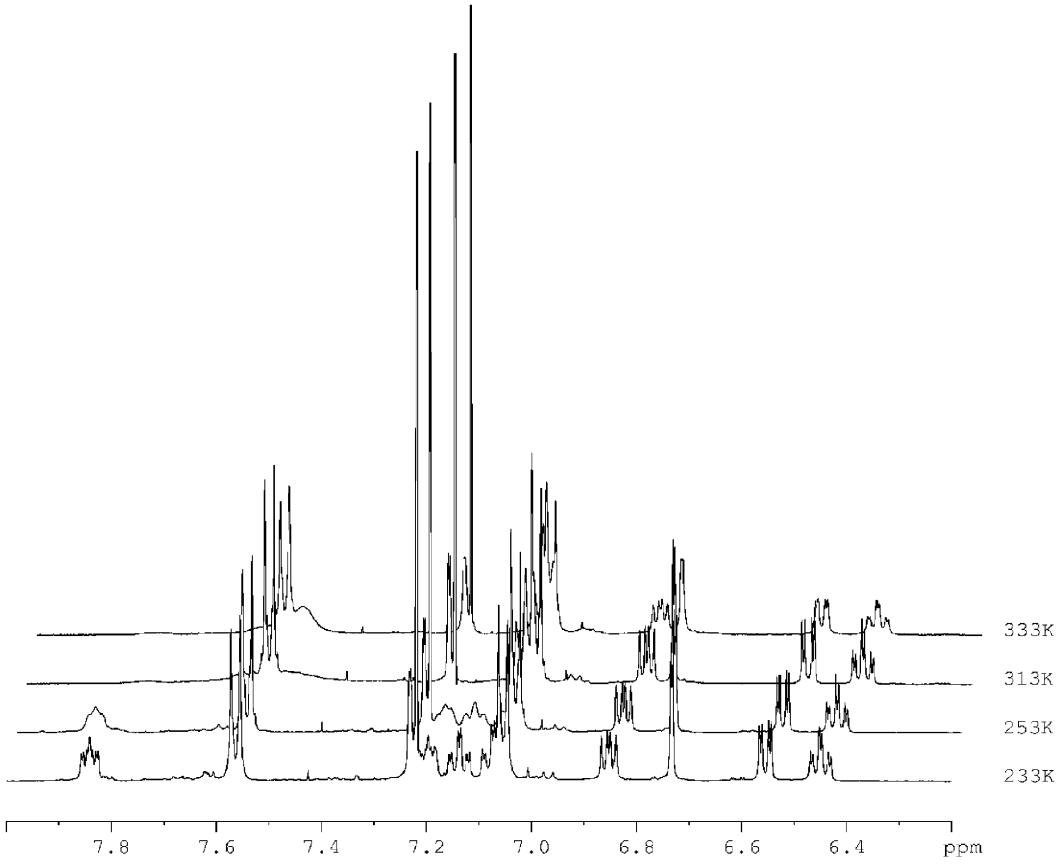

Fig. 3. ^{1}H NMR spectra of complex (**2**).

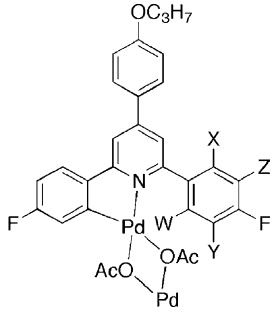

Fig. 4. The labelling system used.

7.1.1. Spectroscopic data

δ_H (RT, $CDCl_3$): 7.54 (4H, d, $J_{(HH)} = 8.5$ Hz, phenoxy ring), 7.25 (12H, v br m, pyridine + non-palladated ring), 7.02 (4H, d, $J_{(HH)} = 8.5$ Hz, phenoxy ring), 6.95 (4H, m, palladated ring), 6.81 (2H, d, $J_{(HH)} = 7.5$ Hz, palladated ring), 6.75 (2H, t, $J_{(HH)} = 7.5$ Hz, palladated ring), 6.60 (2H, d, $^{4}J_{(HH)} = 1.2$ Hz, pyridine ring), 4.02 (4H, t, $J_{(HH)} = 7.0$ Hz, OCH_2), 1.75 (4H, tq, $J_{(HH)} = 7.0$ Hz, OCH_2CH_2), 1.34 (26H, s, AcO + chain), 0.81 (6H, t, $J_{(HH)} = 7.0$ Hz, Me).

δ_C (RT, $CDCl_3$): 177.6, 164.0, 160.6, 156.7, 149.3, 147.6, 144.1, 138.2, 131.3, 127.8, 127.6, 127.2, 126.9, 126.3, 122.3, 121.9, 119.4, 114.2, 112.3, 67.3, 30.8, 28.4, 28.3 28.22, 25.1, 22.1, 21.7, 13.1.

Mass spectrum (LSIMS) *m/z*: 1200 (M^+), 1141 (M^+–AcO)

Elemental analysis: C, 65.8; H, 5.82; N, 2.3; $C_{66}H_{70}N_2O_6Pd_2$ requires C, 66.1; H, 5.9; N, 2.3%.

*7.2. Cyclopalladated dimer (**2**)*

2,6-Bis-(4-fluoro-phenyl)-4-(4-propoxy-phenyl)-pyridine (0.0268 g, 6.67×10^{-5} mol) and palladium acetate (0.0155 g, 6.90×10^{-5} mol) were suspended in acetic acid (25 ml) and heated (65 °C, 48 h). The acetic acid was then removed under vacuum, and the remaining yellow solid dissolved in dichloromethane filtered to remove traces of palladium black. The solvent was removed to give the product (0.0340 g, 3.00×10^{-5} mol, 90%). A single crystal suitable for X-ray diffraction was grown by diffusing methanol into a chloroform solution: the structural data are included as supporting information.

7.2.1. Spectroscopic data

δ_H (RT, $CDCl_3$): 7.56 (4H, d, $J_{(HH)} = 9.0$ Hz, non-fluorinated ring), 7.50 (4H, v br s, non-palladated ring), 7.18 (2H, d, $^{4}J_{(HH)} = 1.8$ Hz, pyridine ring), 7.04 (4H, dd, $J_{(HH)} = 8.8$ Hz, non-palladated ring), 7.02 (4H, d,

$J_{(HH)} = 9.0$ Hz, non-fluorinated ring), 6.80 (2H, dd, $J_{(HH)} = 9.0$ Hz $^4J_{(HF)} = 5.5$ Hz, palladated ring), 6.74 (2H, d, $^4J_{(HH)} = 1.8$ Hz, pyridine ring), 6.55 (2H, dd, $J_{(HF)} = 9.0$ Hz $^4J_{(HH)} = 2.5$ Hz, palladated ring), 6.45 (2H, ddd, $J_{(HH)} = 9.0$ Hz $J_{(HF)} = 9.0$ Hz $^4J_{(HH)} = 2.5$ Hz, palladated ring), 4.03 (4H, t, $J_{(HH)} = 7.0$ Hz, OCH_2), 1.84 (4H, tq, $J_{(HH)} = 7.0$ Hz, OCH_2CH_2), 1.38 (6H, s, AcO), 1.05 (6H, t, $J_{(HH)} = 7.0$ Hz, Me).

At 233 K H_W and H_X appeared as separate peaks at 7.84 and 7.20 ppm, a maximum separation of 323 Hz; they coalesced at 293 K.

At 233 K H_Y and H_Z appeared as separate peaks at 7.14 and 7.07 ppm, a maximum separation of 32 Hz; they coalesced at 268 K.

δ_C (RT, $CDCl_3$): 179.2, 164.2, 163.5 (d, $^1J_{(CF)} = 248$ Hz), 161.0, 160.8, 160.1 (d, $^1J_{(CF)} = 253$ Hz), 152.3 (d, $^3J_{(CF)} = 5.5$ Hz), 149.3, 141.2, 135.2, 128.4, 128.2, 124.2 (d, $^3J_{(CF)} = 8.5$ Hz), 120.0, 118.4 (d, $^2J_{(CF)} = 19$ Hz), 115.4, 115.2 (d, $^2J_{(CF)} = 20$ Hz), 113.3, 110.6 (d, $^2J_{(CF)} = 23.1$ Hz), 69.8, 23.3, 22.6, 10.6.

δ_F (RT, $CDCl_3$): 110.2 (palladated ring), 112.9 (non-palladated ring).

Mass spectrum (LSIMS) *m/z*: 1073 (M^+−AcO), 1012 (M^+−AcO−OC_3H_7)

Elemental analysis: C, 59.0; H, 4.2; N, 2.3; $C_{56}H_{46}F_4N_2O_6Pd_2$ requires C, 59.43; H, 4.10; N, 2.48%.

Acknowledgements

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Appendix A. Supporting information

Experimental data on the crystallographic structures of the unmetallated ligand and compounds (**1**) and (**2**) is included in the supporting information. Full data for their structural analysis for has been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 289395–289397, respectively.

Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK. Fax. (int code) +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.11.066.

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