

# Fluoroalkylated *N*-heterocyclic carbene complexes of palladium

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## Abstract

Fluoroalkylated *N*-heterocyclic carbene complexes of palladium have been synthesized from imidazolium salts and Pd(OAc)<sub>2</sub>. The analogous carbene complexes bearing long alkyl chains have also been prepared. The formation of these carbene complexes proceeds via an intermediate binuclear species, which has been isolated. Complexes such as these may find applications in catalysis in supercritical CO<sub>2</sub> (scCO<sub>2</sub>). © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Carbenes; Fluoroalkylated carbenes; Palladium complexes; X-ray structures

## 1. Introduction

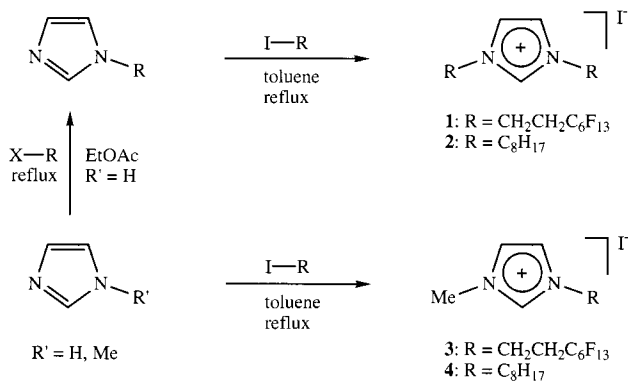
*N*-Heterocyclic carbenes are a novel class of ligands for homogeneous catalysis [1–11]. The metal complexes of these carbenes show high thermal stability and hydrolytic durability because of the strong M–C bonds, which also obviate the need for excess ligands in catalysis. Additional advantages of these ligands over the classic phosphines include easy preparation, easy derivatization and low cost. The 1,3-disubstituted imidazol-2-ylidene complexes of the late transition metals have been used in a number of interesting catalytic reactions such as the Heck and Suzuki reactions [1–3,11], olefin metathesis [4–6], hydrogenation and hydrosilylation [1,10]. A significant example is seen in some palladium ylidene complexes, which display remarkable activity and lifetime in catalysing the Heck olefination of aryl bromides and even the chlorides [1,2,11]. Prompted by the novel features of these carbene ligands, we decided to prepare the supercritical CO<sub>2</sub> (scCO<sub>2</sub>) soluble derivatives in the hope that these carbene ligands can be adapted for catalysis in scCO<sub>2</sub>.

scCO<sub>2</sub> is an attractive alternative to conventional organic liquids for clean synthesis [12]. One of the

major limitations of scCO<sub>2</sub> as a reaction medium for homogeneous catalysis is its rather low solvent strength towards catalysts derived from common organometallic complexes [13–15]. The solubility of a metal complex in scCO<sub>2</sub> can be increased by modification of ligands such that they become ‘CO<sub>2</sub>-philic’. This may be achieved by attaching fluoroalkyl, alkyl or silicone groups to the ligands, which are known to be highly soluble in scCO<sub>2</sub>. A few types of such ligands have been prepared and employed in catalytic reactions in scCO<sub>2</sub>. Examples include fluorinated phosphines, porphyrins, diketonates, alkyl phosphines and phosphites. Fluorinated ligands usually show significantly higher solubility in comparison with other functionalized ligands in scCO<sub>2</sub> [13–15]. However, most of the fluorinated ligands that have been reported so far, such as phosphines bearing fluorinated ponytails [15–20], are not easily accessible and, in the particular case of the phosphines, P–C bond cleavage may occur during a reaction. It is therefore of interest to design and synthesize new CO<sub>2</sub>-philic ligands for the development of catalytic processes in scCO<sub>2</sub>. We report herein on the synthesis and characterization of fluoroalkylated and alkylated imidazol-2-ylidene complexes of palladium. Palladium carbene complexes containing long alkyl chains have recently been reported as thermally stable liquid crystals while this work was in progress [21]. Carbene complexes with other interesting functionalities are also known, but none contain fluorinated substituents [1,22–25].

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Scheme 1. Preparation of imidazolium salts.

## 2. Results and discussion

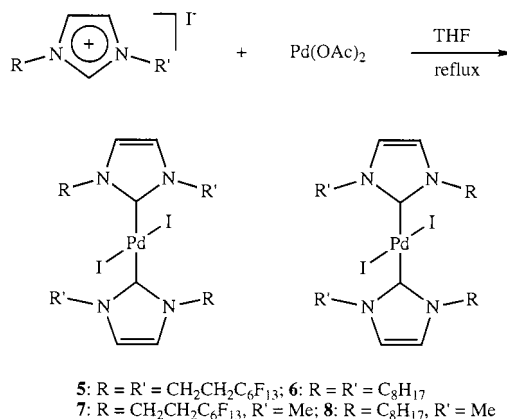
### 2.1. Synthesis of the imidazolium salts

*N*-Heterocyclic carbenes are easily accessible from imidazolium salts, which can in turn be prepared by alkylation of imidazoles [26]. The *N,N'*-difluoroalkyl-substituted imidazolium salt **1** was prepared by alkylation of imidazole with ICH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>F<sub>13</sub>, followed by quaternization of the resultant fluoroalkylimidazole with a second equivalent of the iodide (Scheme 1). The product was obtained in moderate overall yield (50%) on the basis of the iodide, the more expensive of the two reagents. No additional base is necessary in the first step of the reaction, as excess imidazole was used. The *N,N'*-dioctylimidazolium salt **2** was prepared in a similar manner. For the two asymmetrically substituted salts **3** and **4**, the synthesis simply involved one-step alkylation of methylimidazole. The yields of the two alkylated salts **2** and **4** are significantly higher than those for the fluoroalkylated analogues **1** and **3**. This may be due to transformation under the reaction conditions of the fluoroalkyl iodide into other species such as alkenes. Attempts to increase the yields of the reaction by using acetyl-protected imidazole or phase-transfer catalysis met with only slight improvement [27]. Our interest in salts **2** and **4** arises from the fact that normal alkyl groups enhance the solubility of a ligand in scCO<sub>2</sub> as do perfluoroalkyl substituents, albeit to a lesser degree [14]. However, the former is far less expensive. The intervening methylene spacers in **1** and **3** serve to isolate the effect of the electron-withdrawing perfluoroalkyl groups from the ring nitrogen atoms. Theoretical studies indicate that electron donation from the nitrogen to the carbene carbon plays an important role in stabilizing free carbenes and their metal complexes [9,28,29].

### 2.2. Synthesis of the palladium complexes

*N*-Heterocyclic carbene metal complexes can be prepared by ligand substitution reactions using free carbenes, which are accessible via deprotonation of the corresponding imidazolium salts in THF or liquid ammonia [30,31]. An easier, well-established alternative is the direct reaction of the imidazolium salts with metal compounds containing basic ligands [11,25,32,33]. Using this latter approach, the *N,N'*-disubstituted imidazol-2-ylidene complexes of palladium **5–8** have been prepared. A typical synthesis consisted of heating Pd(OAc)<sub>2</sub> with two equivalents of an imidazolium salt in THF for 2 h; the ylidene complexes were isolated as crystalline solids in good yields (Scheme 2). Like many other ylidene complexes, **5–8** are air- and water-stable in solution or as solids [1]. The solubility of these compounds in common organic solvents decreases in the order **6** > **8** > **7** > **5**, with **5** being only scarcely soluble in solvents like THF, acetone or DMSO. The solubility of **5** and **7** in these solvents increases with increasing temperature.

The characterization of these complexes has been accomplished by NMR, MS and microanalysis. The structures of **5** and **7** have been determined by X-ray diffraction (vide infra). The NMR spectra of **5** and **6** are straightforward to interpret and are consistent with the presence of only one isomer in solution. For the two asymmetrically substituted carbene complexes **7** and **8**, NMR spectra suggest the presence of equilibrating rotation isomers, described as *trans-anti* and *trans-syn* on the basis of the relative orientations of the *N*-substituents. Thus, in the case of **7** dissolved in CDCl<sub>3</sub>, the *N*-CH<sub>3</sub> resonance appears initially as one singlet at  $\delta$  3.89 in the <sup>1</sup>H-NMR spectrum. But with time a new peak at  $\delta$  3.97 develops at the expense of the one at  $\delta$  3.89, and the two peaks arrive at a 1:1 ratio after the CDCl<sub>3</sub> solution stands overnight. Based on the structure of **7** revealed by X-ray analysis, the resonance at  $\delta$  3.89 can be assigned to the *N*-CH<sub>3</sub> groups of the *trans-anti* isomer, while the one at the



Scheme 2. Preparation of imidazol-2-ylidene complexes of palladium.

lower field may be attributed to the *trans*–*syn* isomer. Similar observations were made with complex **8**. Rotation isomers have been observed with other biscarbene complexes of palladium, where the carbene ligands are asymmetric and are arranged either *cis* or *trans* around the palladium [25,34]. The *trans* arrangement of the carbenes in **5**–**8** reflects the sterically demanding nature of the long *N*-substituents. In related palladium complexes with sterically less demanding *N*-substituents, both *cis* and *trans* arrangements of the carbene ligands have been reported. However, with bulkier *N*-substituents, the formation of the *trans* isomers appears to be favoured [1,21,22,25]. The electron-withdrawing effect of the perfluoroalkyl fragments in **5** and **7** is not completely eliminated by the methylene spacers, as can be judged by the chemical shifts of the carbene olefinic protons, which appear at lower fields than those of **6** and **8** in the  $^1\text{H-NMR}$  spectra.

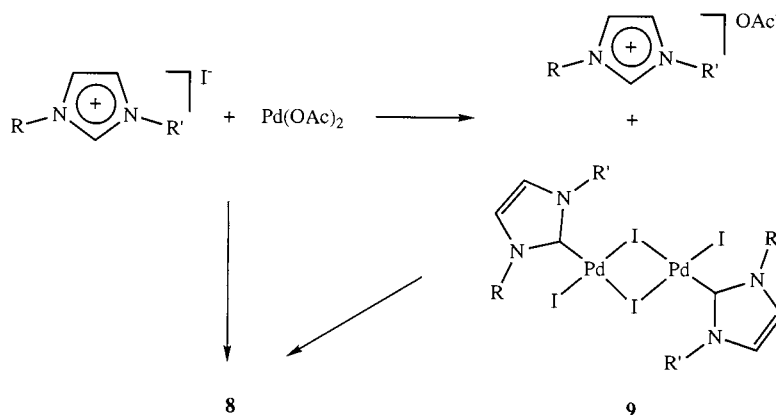
The formation of the complexes **5**–**8** is characterized by a colour change from dark-brown to red and finally to orange, indicating that the reactions may proceed via similar intermediates. Indeed, when the reaction of  $\text{Pd}(\text{OAc})_2$  with the salt **4** was stopped after 5 min, the red binuclear carbene complex **9** was isolated in 90% yield (Scheme 3). The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of **9** resemble those of **8**, except that the carbene carbon in the former comes into resonance at a significantly higher field ( $\delta$  153 versus 168). The binuclear precursors to **5**–**7** may be short lived, and attempted isolation has not been successful. Heating **9** in the presence of **4** and NaOAc in THF converts **9** into **8**, as is expected. An analogous intermediate binuclear species has also been isolated in the preparation of a bisbenzimidazol-2-ylidene complex of mercury [22]. Previously, closely related binuclear carbene complexes of palladium were prepared by reacting  $\text{Pd}(\text{OAc})_2$  with imidazolium salts in the presence of NaI and  $\text{KO}^t\text{Bu}$  [25]. Clearly, Scheme 3 provides an easier route to such binuclear complexes.

As related palladium carbene complexes were shown to be highly effective in Heck reactions [1,2], we examined in preliminary experiments complexes **5**–**8** for the

olefination of 4-bromobenzaldehyde by *n*-butyl acrylate. In DMF, the four complexes were all active, affording the *trans*-cinnamate in >99% yield with 0.5 mol% ylidene complex at 125°C for 12 h reaction time (NaOAc as base). However, in  $\text{scCO}_2$ , under otherwise comparable conditions (200 atm  $\text{CO}_2$ ,  $\text{NEt}_3$  as base), these complexes appear to be less effective, with **5** affording the cinnamate in only 6%, **6** in 10%, **7** in 7% and **8** in 90% yield. While the lower activity of these complexes in  $\text{scCO}_2$  may, to some degree, be related to the much lower polarity of this medium, the reason for the lower activity of **5** and **7** in comparison with their non-fluorinated counterparts is not immediately clear. Solubility does not appear to be the problem, because a homogeneous yellow solution was formed in all the reactions in  $\text{scCO}_2$ . Olefination of iodobenzene catalysed by palladium phosphine complexes in  $\text{scCO}_2$  has recently been reported, where again the reaction tends to be less efficient than in dipolar solvents like DMF [35–37].

### 2.3. Structures of complexes **5** and **7**

Crystal structure determinations of **5** (Fig. 1) and **7** (Fig. 2) show that both complexes have the expected square-planar core geometry, with the palladium atoms located at crystallographic centers of inversion. In both complexes the carbene ligands are *trans* arranged and, in **7**, they are *trans*–*anti* configured. The mean planes of the  $\text{C}_3\text{N}_2$  rings of the ylidene ligands are tilted by 86.6° in **5** (80.5° in **7**) with respect to the square-planar environment of Pd1, thus minimizing steric interactions between the *N*-substituents and iodides [21]. The Pd–C bond lengths of 2.040(8)° in **5** and 2.041(10)° in **7**, respectively, are comparable with values found in other palladium carbene complexes (Table 1) [1,11,21,22,24,25]. Within the solid state the fluorinated alkyl chains of neighbouring molecules are aligned in a parallel fashion.  $\text{C}_6\text{F}_{13}$  chains in **5** are stacked intra- as well as intermolecularly in a ‘head-to-head’ pattern resulting in molecular stacks (Fig. 3), whereas the monosubsti-



Scheme 3. Formation of **8** via binuclear complex **9** ( $\text{R} = \text{C}_8\text{H}_{17}$ ,  $\text{R}' = \text{Me}$ ).

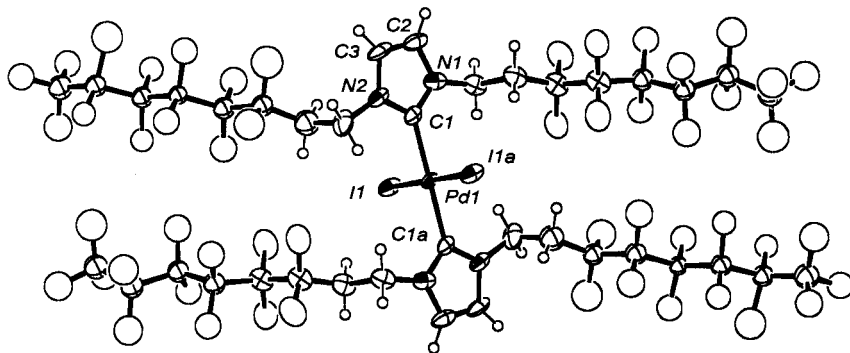


Fig. 1. Molecular structure of **5** in the solid state showing 50% probability thermal ellipsoids.

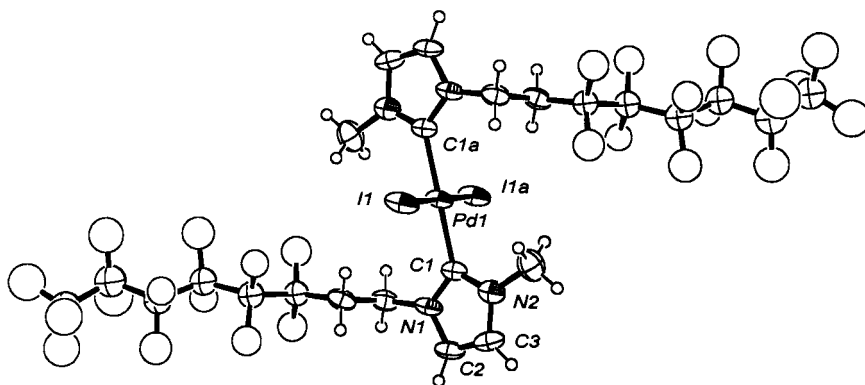


Fig. 2. Molecular structure of **7** in the solid state showing 50% probability thermal ellipsoids.

tuted ligands in **7** show an intermolecular ‘head-to-tail’ pattern, which results in a zigzag arrangement (Fig. 4).

In summary, fluoroalkylated and alkylated imidazolium salts and the corresponding carbene complexes have been prepared. In contrast to fluorophosphines, fluorinated *N*-heterocyclic carbenes and their metal complexes are easy to prepare and require no special handling precautions, and thus provide an easy entry to soluble catalysts for reactions in *scCO*<sub>2</sub>. While the activity of the *N*-substituted imidazol-2-ylidene complexes of palladium appears to be low in the Heck reaction in *scCO*<sub>2</sub>, complexes like these may find applications in other reactions in this medium or in fluoros phase catalysis.

### 3. Experimental

The solvents were degassed and dried before use. All the reagents were used as received. NMR spectra were recorded on a Gemini 300 spectrometer at 300.10 (<sup>1</sup>H) and 75.46 MHz (<sup>13</sup>C) in ppm with reference to TMS internal standard in CDCl<sub>3</sub>, unless otherwise indicated. Abbreviations for NMR spectral multiplicities: s = singlet, t = triplet, m = multiplet, br = broad. Elemental analyses were performed by the Microanalysis Laboratory, Department of Chemistry, at the University of Liverpool, and Butterworth Laboratories Ltd. Mass

spectra were recorded on a VG7070E mass spectrometer.

X-ray data were collected on a Stoe IPDS image plate diffractometer using Mo-K<sub>α</sub> radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and a graphite monochromator. Crystals of **5** and **7** were obtained from crystallization in acetone and CH<sub>2</sub>Cl<sub>2</sub>–hexane, respectively. The crystals were

Table 1  
Selected bond lengths (Å) and angles (°) for **5** and **7**

	<b>5</b>	<b>7</b>
<i>Bond lengths</i>		
Pd(1)–C(1)	2.040(8)	2.041(10)
Pd(1)–I(1)	2.5982(8)	2.5969(8)
C(1)–N(1)	1.339(11)	1.332(12)
C(1)–N(2)	1.346(11)	1.345(12)
N(1)–C(2)	1.372(12)	1.383(13)
N(2)–C(3)	1.382(12)	1.368(13)
C(2)–C(3)	1.330(15)	1.335(15)
<i>Bond angles</i>		
C(1)–Pd(1)–I(1)	91.4(2)	88.9(2)
C(1)–Pd(1)–C(1a)	180	180
I(1)–Pd(1)–I(1a)	180	180
N(1)–C(1)–N(2)	105.1(7)	105.4(9)
C(1)–N(1)–C(2)	110.5(8)	110.5(9)
C(1)–N(2)–C(3)	110.4(8)	110.4(9)
N(1)–C(2)–C(3)	107.4(9)	106.5(9)
N(2)–C(3)–C(2)	106.4(9)	107.1(9)

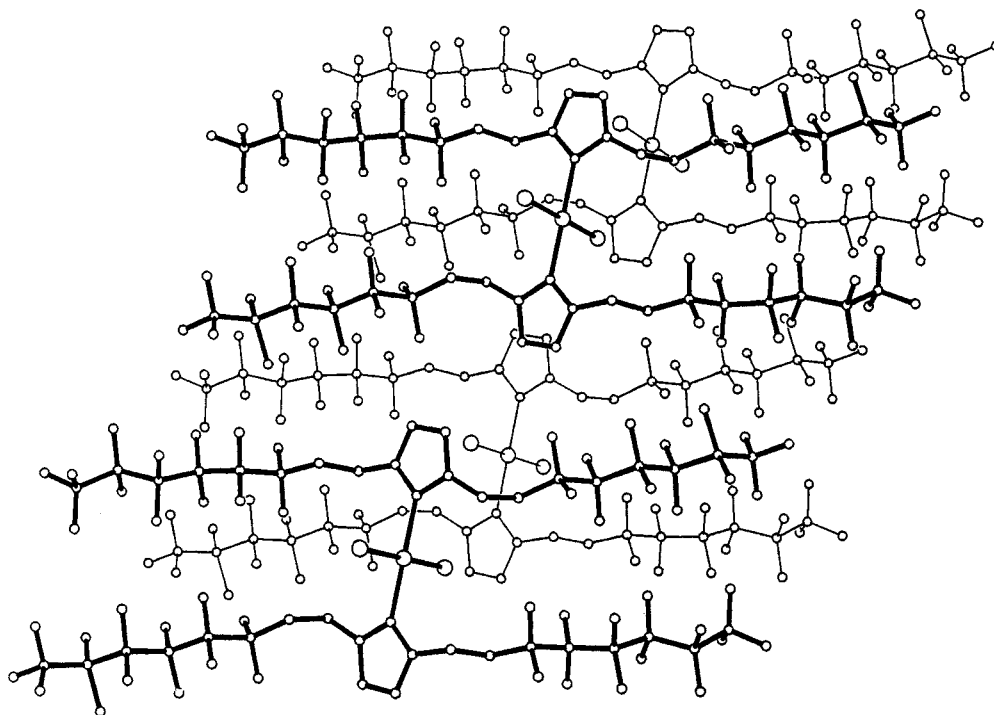


Fig. 3. Packing arrangement of 5 in the solid state viewing along the [110] vector.

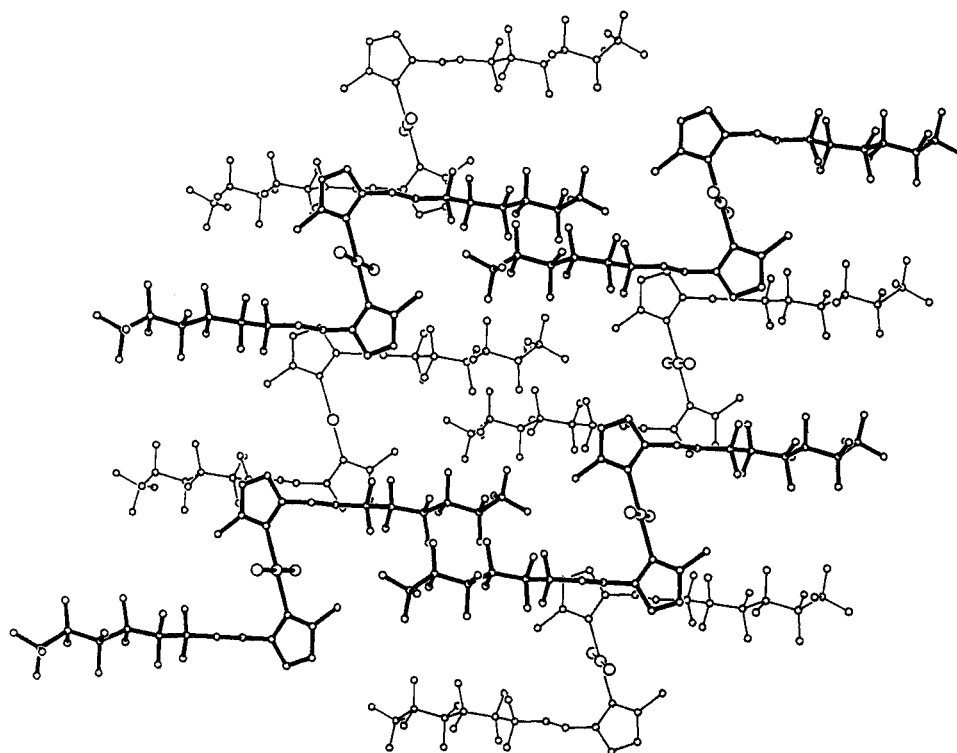


Fig. 4. Packing arrangement of 5 in the solid state viewing along the [010] vector.

coated with Nujol, mounted on glass fibres and held at 200 K. The structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  using all

data [38]. Fluoroalkyl chains of both structures show conformational disorder. Disordered atoms were split in two positions and refined isotropically using distance

and similar *U* restraints. All other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the calculated positions. Crystallographic details for both structures are shown in Table 2.

### 3.1. 1,3-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)imidazolium iodide (**1**)

Imidazole (1.702 g, 0.025 mol) and 1*H*,1*H*,2*H*,2*H*-perfluorooctyl iodide (4.740 g, 0.010 mol) were dissolved in 30 ml of ethyl acetate. The mixture was refluxed overnight under argon. After cooling to room temperature, the imidazolium salt formed in the reaction and unreacted imidazole were extracted with water, and the solvent removed in vacuo. To the residue and 1*H*,1*H*,2*H*,2*H*-perfluorooctyl iodide (4.740 g, 0.010 mol) was then added 30 ml of toluene. The mixture was refluxed overnight under argon, during which time the product precipitated out as a white solid. The precipitate was separated, dried in vacuo, and finally crystallized from CH<sub>3</sub>CN–toluene affording **1** as a white crystalline solid (4.480 g, 50%, based on the iodide). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>): δ 9.44 (s, 1H, N<sub>2</sub>CH), 7.94 (s, 2H, NCH), 4.61 (t, <sup>3</sup>*J*<sub>HH</sub> = 5 Hz, 4H, NCH<sub>2</sub>), 2.99 (br t, <sup>3</sup>*J*<sub>HF</sub> = 19 Hz, 4H, CH<sub>2</sub>CF<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (DMSO): δ 137.7 (N<sub>2</sub>CH), 123.1 (NCH), 41.8 (NCH<sub>2</sub>), 30.2 (NCH<sub>2</sub>CH<sub>2</sub>). MS (FAB): *m/z* 761 ([M<sup>+</sup> – I], 100). Anal. Calc. for C<sub>19</sub>H<sub>11</sub>N<sub>2</sub>F<sub>26</sub>I (888.17): C, 25.69; H, 1.25; N, 3.15. Found: C, 26.05; H, 1.48; N, 3.35%.

### 3.2. 1,3-Dioctylimidazolium iodide (**2**)

The procedure was similar to that for **1**. Starting from imidazole (1.360 g, 0.020 mol) and octyl bromide (1.550 g, 0.008 mol) and following quaternization with octyl iodide (2.400 g, 0.010 mol), **2** was obtained as a yellow oil (3.030 g, 90%, based on the bromide). <sup>1</sup>H-NMR: δ 10.28 (s, 1H, N<sub>2</sub>CH), 7.62 (d, <sup>4</sup>*J*<sub>HH</sub> = 1.5 Hz, 2H, NCH), 4.39 (t, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 4H, NCH<sub>2</sub>), 1.94 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 1.35–1.22 (m, 20H, CH<sub>2</sub>), 0.83 (t, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR: δ 135.8 (N<sub>2</sub>CH), 122.2 (NCH), 49.8 (NCH<sub>2</sub>), 31–22 (CH<sub>2</sub>), 13.6 (CH<sub>3</sub>). MS (FAB): *m/z* 293 ([M<sup>+</sup> – I], 100). Anal. Calc. for C<sub>19</sub>H<sub>37</sub>N<sub>2</sub>I (420.42): C, 54.28; H, 8.87; N, 6.66. Found: C, 53.78; H, 8.95; N, 6.53%.

### 3.3. 1-Methyl-3-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)imidazolium iodide (**3**)

1-Methylimidazole (1.640 g, 0.020 mol) and 1*H*,1*H*,2*H*,2*H*-perfluorooctyl iodide (10.428 g, 0.022 mol) were dissolved in 30 ml of toluene. The mixture was refluxed overnight, during which time an oily precipitate formed. The solvent was removed in vacuo, and the precipitate crystallized from CH<sub>3</sub>CN–toluene affording **3** as white crystals (7.080 g, 67%, based on

Table 2  
Crystal data and structure refinement for **5** and **7**

	<b>5</b>	<b>7</b>
Empirical formula	C <sub>38</sub> H <sub>20</sub> F <sub>52</sub> I <sub>2</sub> N <sub>4</sub> Pd	C <sub>24</sub> H <sub>18</sub> F <sub>26</sub> I <sub>2</sub> N <sub>4</sub> Pd
Formula weight	1880.82	1216.66
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Unit cell dimensions		
<i>a</i> (Å)	7.3660(11)	16.333(3)
<i>b</i> (Å)	8.9609(14)	8.994(2)
<i>c</i> (Å)	21.651(4)	14.160(3)
$\alpha$ (°)	98.74(2)	90
$\beta$ (°)	91.06(2)	113.68(3)
$\gamma$ (°)	96.06(2)	90
<i>V</i> (Å <sup>3</sup> )	1403.8(4)	1905.0(7)
<i>Z</i>	1	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.225	2.121
$\mu$ (Mo–K $\alpha$ ) (mm <sup>-1</sup> )	1.492	2.078
<i>F</i> (000)	896	1152
<i>T</i> (K)	200(2)	200(2)
$\lambda$ (Å)	0.71073	0.71073
Reflections collected	8899	5313
Reflections independent	4141	2846
<i>R</i> <sub>int</sub>	0.035	0.053
2 $\theta$ Range	3.8–48.3	5.3–48.1
Completeness (%)	91.8	88.3
<i>R</i> <sub>1</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.065	0.057
<i>wR</i> <sub>2</sub> (all data)	0.189	0.145
Largest difference peak and hole (e Å <sup>-3</sup> )	1.432 and –1.619	1.565 and –1.315

1-methylimidazole). <sup>1</sup>H-NMR: 10.16 (s, 1H, N<sub>2</sub>CH), 7.62 (t, *J*<sub>HH</sub> = 1.5 Hz, 1H, NCH), 7.47 (t, *J*<sub>HH</sub> = 1.5 Hz, 1H, NCH), 4.86 (t, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 2H, NCH<sub>2</sub>), 4.09 (s, 3H, NCH<sub>3</sub>), 2.99 (m, 2H, CH<sub>2</sub>CF<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR: δ 138.0 (N<sub>2</sub>CH), 123.6 (NCH), 122.9 (NCH), 42.7 (NCH<sub>2</sub>), 37.3 (NCH<sub>3</sub>), 32.0 (NCH<sub>2</sub>CH<sub>2</sub>). MS (FAB): *m/z* 429 ([M<sup>+</sup> – I], 100). Anal. Calc. for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>F<sub>13</sub>I.H<sub>2</sub>O (574.12): C, 25.10; H, 2.11; N, 4.88. Found: C, 25.19; H, 1.81; N, 4.87%.

### 3.4. 1-Methyl-3-octylimidazolium iodide (**4**)

The procedure was similar to that for **3**. Starting from 1-methylimidazole (1.650 g, 0.020 mol) and 1-iodooctane (5.310 g, 0.022 mol), **4** was obtained as a yellow oil (5.830 g, 90%, based on 1-methylimidazole). <sup>1</sup>H-NMR: δ 9.96 (s, 1H, N<sub>2</sub>CH), 7.74 (t, *J*<sub>HH</sub> = 1.8 Hz, 1H, NCH), 7.63 (t, *J*<sub>HH</sub> = 1.8 Hz, 1H, NCH), 4.36 (t, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 2H, NCH<sub>2</sub>), 4.15 (s, 3H, NCH<sub>3</sub>), 1.94 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 1.35–1.22 (m, 10H, CH<sub>2</sub>), 0.83 (t, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR: δ 136.5 (N<sub>2</sub>CH), 123.9 (NCH), 122.3 (NCH), 50.1 (NCH<sub>2</sub>), 37.1 (NCH<sub>3</sub>), 31–22 (CH<sub>2</sub>), 13.9 (CH<sub>3</sub>). MS (FAB): *m/z* 195 ([M<sup>+</sup> – I], 100). Anal. Calc. for C<sub>12</sub>H<sub>23</sub>N<sub>2</sub>I (322.23): C, 44.73; H, 7.19; N, 8.69. Found: C, 44.64; H, 7.35; N, 8.57%.

### 3.5. Bis[1,3-bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)imidazol-2-ylidene]diiodopalladium(II) (**5**)

Complex **5** was prepared using previously established procedures [11,25]. In a typical experiment, the imidazolium salt **1** (460 mg, 0.52 mmol) and palladium acetate (55 mg, 0.25 mmol) were dissolved in 20 ml of THF. After refluxing for 2 h under argon, the mixture was filtered through a pad of silica gel. The solvent was then removed in vacuo, and the residue crystallized from hot acetone to give **5** as orange crystals (343 mg, 73%). <sup>1</sup>H-NMR (200 MHz, acetone-*d*<sub>6</sub>): δ 7.52 (s, 4H, NCH), 4.83 (t, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 8H, NCH<sub>2</sub>), 3.12 (br m, 8H, CH<sub>2</sub>CF<sub>2</sub>). MS (FAB): *m/z* 1753 ([M<sup>+</sup> – I], 2.5). Anal. Calc. for C<sub>38</sub>H<sub>20</sub>N<sub>4</sub>F<sub>52</sub>I<sub>2</sub>Pd (1880.82): C, 24.27; H, 1.07; N, 2.98. Found: C, 24.32; H, 0.89; N, 2.83%.

### 3.6. Bis(1,3-dioctylimidazol-2-ylidene)diiodopalladium(II) (**6**)

Complex **6** was prepared using the same procedure as for **5** except that palladium acetate (87 mg, 0.39 mmol) was reacted with the imidazolium salt **2** (340 mg, 0.81 mmol). Yellow crystals of **6** were obtained from crystallization in pentane (314.0 mg, 85%). <sup>1</sup>H-NMR: δ 6.87 (s, 4H, NCH), 4.35 (t, <sup>3</sup>*J*<sub>HH</sub> = 8 Hz, 8H, NCH<sub>2</sub>), 2.04 (m, 8H, NCH<sub>2</sub>CH<sub>2</sub>), 1.39–1.25 (m, 40H, CH<sub>2</sub>), 0.88 (t, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 12H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR: δ 167.1 (N<sub>2</sub>C), 120.9 (NCH), 51.5 (NCH<sub>2</sub>), 31–22 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>). MS (FAB): *m/z* 817 ([M<sup>+</sup> – I], 1.3). Anal. Calc. for C<sub>38</sub>H<sub>72</sub>N<sub>4</sub>I<sub>2</sub>Pd (945.24): C, 48.29; H, 7.68; N 5.93. Found: C, 48.07; H, 7.69; N, 5.82%.

### 3.7. Bis[1-methyl-3-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)imidazol-2-ylidene]diiodopalladium(II) (**7**)

Complex **7** was prepared using the same procedure as for **5** except that palladium acetate (206 mg, 0.92 mmol) was reacted with the imidazolium salt **3** (1020 mg, 1.93 mmol). Orange crystals of **7** were obtained from crystallization in CH<sub>2</sub>Cl<sub>2</sub>–hexane (851 mg, 76%). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ 6.93 (s, 4H, NCH), 4.67 (m, 4H, NCH<sub>2</sub>), 3.89 (s, 6H, NCH<sub>3</sub>), 2.94 (br m, 4H, CH<sub>2</sub>CF<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR: δ 168.8 (N<sub>2</sub>C), 123.6 (NCH), 122.4 (NCH). MS (FAB): *m/z* 1089 ([M<sup>+</sup> – I], 4.2). Anal. Calc. for C<sub>24</sub>H<sub>18</sub>N<sub>4</sub>F<sub>26</sub>I<sub>2</sub>Pd (1216.66): C, 23.69; H, 1.49; N 4.61. Found: C, 23.67; H, 1.26; N, 4.55%.

### 3.8. Bis(1-methyl-3-octylimidazol-2-ylidene)diiodopalladium(II) (**8**)

Compound **8** was prepared using the same procedure as for **5**, but starting from palladium acetate (187 mg, 0.83 mmol) and the imidazolium salt **4** (563 mg, 1.75 mmol). Yellow crystals of **8** were obtained from crystallization in CH<sub>2</sub>Cl<sub>2</sub>–pentane (559 mg, 90%). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ 6.86 (s, 4H, NCH), 4.32 (t, 4H,

<sup>3</sup>*J*<sub>HH</sub> = 7 Hz, NCH<sub>2</sub>), 3.95 (s, 6H, NCH<sub>3</sub>), 2.04 (br m, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 1.36–1.27 (m, 20H, CH<sub>2</sub>), 0.88 (t, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (75 MHz): δ 167.7 (N<sub>2</sub>C), 122.3 (NCH), 121.0 (NCH), 51.3 (NCH<sub>2</sub>), 38.4 (NCH<sub>3</sub>), 31–22 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>). MS (FAB): *m/z* 621 ([M<sup>+</sup> – I], 2.5). Anal. Calc. for C<sub>24</sub>H<sub>44</sub>N<sub>4</sub>I<sub>2</sub>Pd (748.87): C, 38.49; H, 5.9; N 7.5. Found: C, 38.46; H, 5.87; N, 7.44%.

### 3.9. Bis(1-methyl-3-octylimidazol-2-ylidene)diiodo-μ'-diiododipalladium(II) (**9**)

Palladium acetate (100 mg, 0.45 mmol) and the imidazolium salt **4** (302 mg, 0.94 mmol) were dissolved in 20 ml of THF. After stirring for 1 or 2 min at reflux, the initially dark-brown solution turned red. The reaction was stopped after 5 min. The red solution was cooled to room temperature and filtered through a pad of silica gel. The solvent was then removed under vacuo. Crystallization in toluene–hexane afforded **9** as a red crystalline solid (224 mg, 90%). <sup>1</sup>H-NMR: δ 6.95 (s, 4H, NCH), 4.39 (br m, 4H, NCH<sub>2</sub>), 4.02 (s, 6H, NCH<sub>3</sub>), 2.02 (br m, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 1.44–1.31 (m, 20H, CH<sub>2</sub>), 0.90 (t, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR: δ 153.0 (N<sub>2</sub>C), 123.6 (NCH), 122.1 (NCH), 51.7 (NCH<sub>2</sub>), 39.1 (NCH<sub>3</sub>), 31–22 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>). Anal. Calc. for C<sub>24</sub>H<sub>44</sub>N<sub>4</sub>I<sub>4</sub>Pd<sub>2</sub> (1109.10): C, 25.99; H, 4.00; N 5.05. Found: C, 26.49; H, 4.02; N, 4.86%.

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 135358 for compound **5** and CCDC 135359 for compound **7**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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