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Journal of Organometallic Chemistry 683 (2003) 240–248

Journal  
of Organo  
metallic  
Chemistry[www.elsevier.com/locate/jorganchem](http://www.elsevier.com/locate/jorganchem)

# Photochemical synthesis of a palladium dichloromethyl complex, $\{(\text{hexyl})\text{HC}(\text{N-methyl-imidazol-2-yl})_2\}\text{Pd}(\text{CHCl}_2)\text{Cl}$ . X-ray molecular structures of $\{(\text{hexyl})\text{HC}(\text{N-methylimidazolyl-2-yl})_2\}\text{Pd}(\text{X})\text{Cl}$ , $\text{X} = \text{Cl}$ , and $\text{CHCl}_2$

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Received 7 April 2003; received in revised form 3 July 2003; accepted 14 July 2003

## Abstract

The reaction of  $(\text{hexyl})\text{HC}(\text{mim})_2$  (**1**,  $\text{mim} = N\text{-methyl-imidazol-2-yl}$ ) with  $(\text{cod})\text{PdMeCl}$  in  $\text{C}_6\text{H}_6$  yields  $\{(\text{hexyl})\text{HC}(\text{mim})_2\}\text{Pd}(\text{Me})\text{Cl}$  (**3**). The photochemical reaction of **3** with  $\text{CH}_2\text{Cl}_2$  at  $23^\circ\text{C}$  in ambient room light yields  $\{(\text{hexyl})\text{HC}(\text{mim})_2\}\text{Pd}(\text{CHCl}_2)\text{Cl}$  (**4**). It is proposed that this reaction proceeds by homolytic scission of the  $\text{Pd-Me}$  bond of **3**.

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**Keywords:** Photochemical synthesis; Palladium dichloromethyl complexes; Molecular structures

## 1. Introduction

Metal-catalyzed insertion polymerization of vinyl halides is a challenging goal. Previously we showed that single-site olefin polymerization catalysts based on early or late transition metals undergo facile net 1,2 insertion of vinyl chloride (VC), but the resulting  $\text{L}_n\text{MCH}_2\text{CHRCl}$  species undergo rapid  $\beta\text{-Cl}$  elimination to form  $\text{L}_n\text{MCl}$  products and  $\text{CH}_2=\text{CHR}$  olefins, which precludes insertion polymerization [1]. Similar 1,2 insertion/ $\beta\text{-X}$  elimination reactions of  $\text{CH}_2=\text{CHX}$  ( $\text{X} = \text{F}$ ,  $\text{Cl}$ ,  $\text{Br}$ ) with metal hydrides or discrete or in situ-generated metal alkyl species have been reported [2]. An alternative approach to the insertion polymerization of VC would involve chain growth by 2,1 insertion, so that intermediate  $\alpha\text{-Cl}$ -substituted  $\text{L}_n\text{MCHClCH}_2\text{R}$  alkyl species are generated. As part of an effort to assess the viability of 2,1 VC insertion polymerization, we are studying the chemistry of metal alkyls with  $\alpha$ -halogen substituents. Here we describe the synthesis and structure of a new Pd dichloromethyl complex

$\{(\text{hexyl})\text{HC}(\text{mim})_2\}\text{Pd}(\text{CHCl}_2)\text{Cl}$  ( $\text{mim} = N\text{-methyl-imidazol-2-yl}$ ). Metal alkyls containing  $\alpha$ -halogen substituents are quite common [3–5]. In particular, transition metal  $\text{MCHCl}_2$  complexes [6–16] and main group  $\text{MCHCl}_2$  compounds [17–19] have been synthesized previously, typically by oxidative addition of  $\text{CHCl}_3$  to low valent precursors or by alkylation of metal halides by  $\text{LiCHCl}_2$  [20].

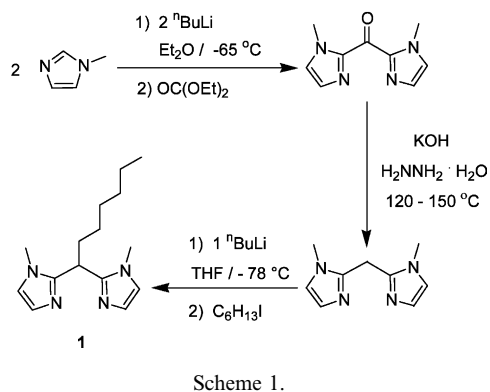
## 2. Results and discussion

### 2.1. Ligand synthesis

The neutral bis-imidazole ligand  $(\text{hexyl})\text{HC}(\text{mim})_2$  (**1**) was prepared as shown in Scheme 1. Deprotonation of  $N$ -methylimidazole ( $\text{mim}$ ) with  $n\text{-BuLi}$  at  $-65^\circ\text{C}$  followed by addition of diethyl carbonate yields  $(\text{mim})_2\text{CO}$  [21]. Reduction of  $(\text{mim})_2\text{CO}$  to  $(\text{mim})_2\text{CH}_2$  with  $\text{KOH}$  in  $\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$  [22], followed by deprotonation with  $n\text{-BuLi}$  ( $-78^\circ\text{C}$ , 2 h) and quenching with 1-iodohexane ( $-78$ – $23^\circ\text{C}$ ) produces **1** as a white solid in 92% yield [23].

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## 2.2. Synthesis of $\{(hexyl)HC(mim)_2\}PdCl_2$ and $\{(hexyl)HC(mim)_2\}PdClMe$

The reaction of **1** with  $(cod)PdCl_2$  ( $cod = 1,5$ -cyclooctadiene) in  $CH_2Cl_2$  yields  $\{(hexyl)HC(mim)_2\}PdCl_2$  (**2**, Scheme 2) as an orange solid. In contrast to earlier bis(imidazolyl)methane complexes, **2** is highly soluble in  $CH_2Cl_2$  due to the hexyl substituent [24]. Similarly, the reaction of **1** with  $(cod)Pd(Me)Cl$  in benzene yields  $\{(hexyl)HC(mim)_2\}Pd(Me)Cl$  (**3**, Scheme 2) as an off-white solid. Complex **3** is soluble in  $CH_2Cl_2$  and  $CH_2ClCH_2Cl$ , sparingly soluble in  $C_6H_5Cl$ , and insoluble in benzene and toluene.

## 2.3. Molecular structure of $\{(hexyl)HC(mim)_2\}PdCl_2$ (**2**)

The molecular structure of **2** was determined by X-ray diffraction. ORTEP views of **2** are shown in Fig. 1. The crystallographic data and a list of selected bond distances and angles for **2** are given in Tables 1 and 2, respectively. Compound **2** adopts a square planar structure about palladium as expected. The sum of the angles at Pd =  $360.0^\circ$ , and the Pd lies 0.01 Å out of the N–N–Cl–Cl plane. The (N(5)–Pd–N(6)) angle is

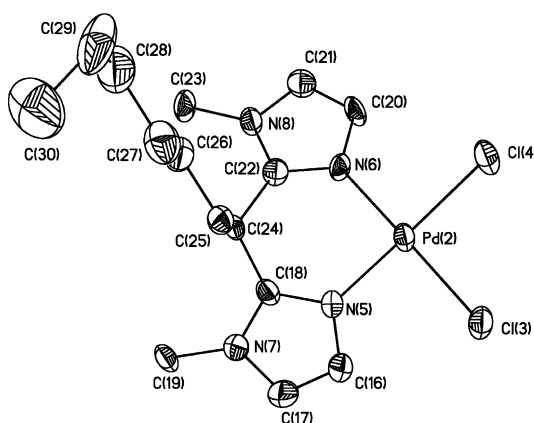
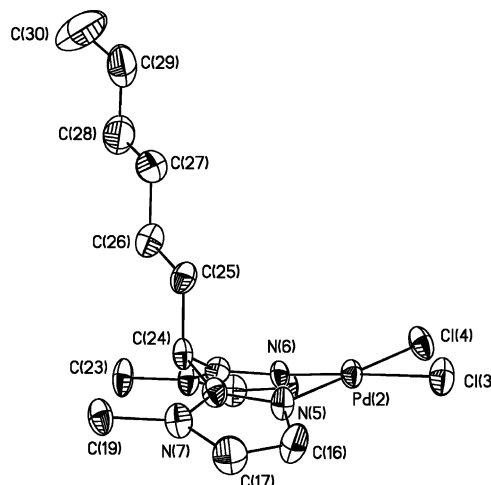
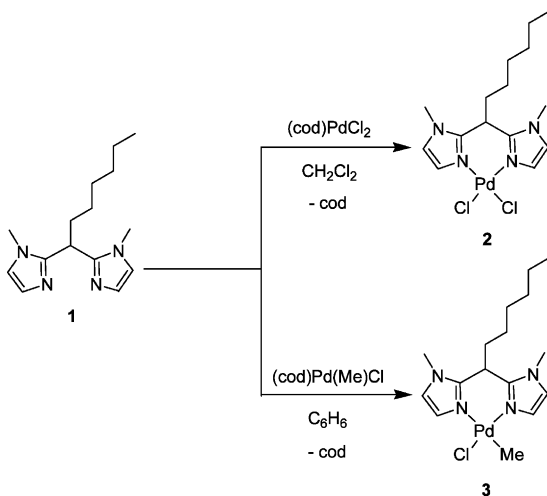


Fig. 1. Two views of the molecular structure of  $\{(hexyl)HC(mim)_2\}PdCl_2$  (**2**). Hydrogen atoms are omitted.

$88.2(2)^\circ$ , and the other angles at Pd are close to  $90^\circ$ . The chelate ring adopts a boat conformation. The angle between the N–C–C–N and N–Pd–N planes (N(6)–C(22)–C(18)–N(5)/N(5)–Pd(2)–N(6)) is  $161.46^\circ$ , and the angle between the N–C–C–N and C–C–C planes (N(6)–C(22)–C(18)–N(5)/C(18)–C(24)–C(22)) is  $147.20^\circ$ . Overall, the structure **2** is very similar to those of the bis(pyrazolyl)methane complexes  $\{Me_2C(pz)_2\}PdCl_2$  and  $\{Ph_2C(pz)_2\}PdCl_2$  [25,26].

The  $^1H$ -NMR spectrum of **2** at  $25^\circ C$  contains one set of imidazolyl H4 ( $\delta$  7.43) and H5 ( $\delta$  6.88) resonances and one set of hexyl resonances, which is consistent with the  $C_s$ -symmetric structure observed in the solid state. The NOESY spectrum of **2** contains crosspeaks between the imidazolyl N–Me resonance and the bridgehead methine resonance, which is consistent with placement of the hexyl group in the apical position, as observed in the solid state. This conformation minimizes steric repulsion between the N–Me groups and the hexyl group. Previously, Canty proposed an analogous structure for  $\{MeHC(mim)_2\}PdMe_2$  based on NMR and molecular modeling studies [27].

Table 1  
Crystal data and structure refinement for **2** and **4**

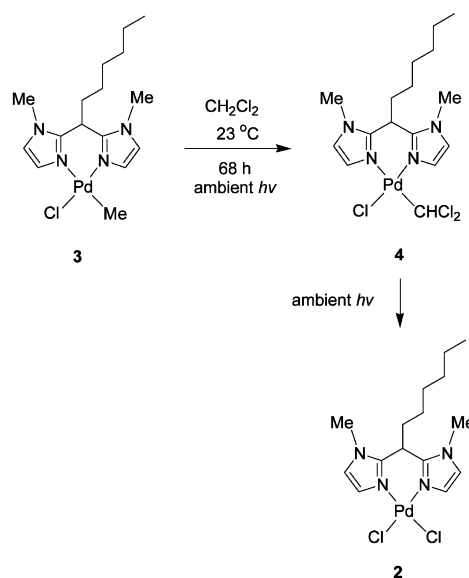
Complex	<b>2</b> ·2 CH <sub>2</sub> Cl <sub>2</sub>	<b>4</b>
Empirical formula	C <sub>30</sub> H <sub>48</sub> Cl <sub>4</sub> N <sub>8</sub> Pd <sub>2</sub> + 2CH <sub>2</sub> Cl <sub>2</sub>	C <sub>16</sub> H <sub>25</sub> Cl <sub>3</sub> N <sub>4</sub> Pd
Formula weight	1021.04 (including solvent)	486.15
Temperature (K)	100	130
Wavelength (Å)	Mo–K <sub>α</sub> , 0.71073	Mo–K <sub>α</sub> , 0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	16.355(5)	9.650(2)
<i>b</i> (Å)	13.834(4)	15.865(3)
<i>c</i> (Å)	19.066(6)	12.751(2)
$\beta$ (°)	93.475(6)	94.440(3)
<i>V</i> (Å <sup>3</sup> )	4306(2)	1946.4(6)
<i>Z</i>	4	4
<i>D</i> <sub>calc</sub> (mg m <sup>-3</sup> )	1.575	1.659
$\mu$ , mm <sup>-1</sup>	1.326	1.371
Crystal size (mm)	0.45 × 0.20 × 0.07	0.15 × 0.10 × 0.10
2 $\theta$ range (°)	1.82–25.03	2.48–25.03
Limiting indices	–19 ≤ <i>h</i> ≤ 15, –16 ≤ <i>k</i> ≤ 13, –19 ≤ <i>l</i> ≤ 22	–6 ≤ <i>h</i> ≤ 11, –18 ≤ <i>k</i> ≤ 18, –15 ≤ <i>l</i> ≤ 15
Reflections collected	20 562	9723
Independent reflections	7586	3433
<i>R</i> <sub>int</sub>	0.0294	0.0205
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	7586/0/462	3433/0/220
Adsorption correction	SADABS based on redundant diffractions	SADABS based on redundant diffractions
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0689, <i>wR</i> <sub>2</sub> = 0.1720	<i>R</i> <sub>1</sub> = 0.0527, <i>wR</i> <sub>2</sub> = 0.1482
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0749, <i>wR</i> <sub>2</sub> = 0.1754	<i>R</i> <sub>1</sub> = 0.0536, <i>wR</i> <sub>2</sub> = 0.1489
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.152	1.196
Largest difference peak and hole (e Å <sup>-3</sup> )	2.911 and –0.986	1.073 and –1.330
Diffractometer	Bruker SMART APEX	Bruker SMART APEX

#### 2.4. Generation of {(hexyl)HC(mim)<sub>2</sub>}Pd(CHCl<sub>2</sub>)Cl (**4**)

Complex **3** is stable in CH<sub>2</sub>Cl<sub>2</sub> at 23 °C, but only if protected from light through the use of amberized glassware or storage of the solution in the dark. Exposure of a CH<sub>2</sub>Cl<sub>2</sub> solution of **3** to ambient room light for 68 h at 23 °C results in complete disappearance of **3** and formation of a 95/5 mixture of {(hexyl)HC(mim)<sub>2</sub>}Pd(CHCl<sub>2</sub>)Cl (**4**) and dichloride complex **2** (Scheme 3) [28]. Small amounts of crystalline **4** were obtained by recrystallization of the product mixture from CH<sub>2</sub>Cl<sub>2</sub>–pentane, which enabled X-ray crystallographic analysis of **4**. Further exposure of the solution to room light results in complete conversion to **2**.

Table 2  
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths			
Cl(3)–Pd(2)	2.308(6)	Cl(4)–Pd(2)	2.290(1)
N(5)–Pd(2)	2.014(5)	N(6)–Pd(2)	2.009(5)
N(5)–C(18)	1.336(8)	N(6)–C(22)	1.334(8)
C(18)–C(24)	1.499(9)	C(22)–C(24)	1.503(9)
Bond angles			
N(5)–Pd(2)–N(6)	88.2(2)	C(16)–N(5)–Pd(2)	127.1(5)
N(5)–Pd(2)–Cl(3)	90.8(2)	C(18)–N(5)–Pd(2)	125.7(5)
N(6)–Pd(2)–Cl(3)	178.0(2)	N(5)–C(18)–N(7)	109.1(6)
N(5)–Pd(2)–Cl(4)	178.8(2)	N(5)–C(18)–C(24)	125.8(6)
N(6)–Pd(2)–Cl(4)	90.6(2)	N(7)–C(18)–C(24)	125.0(6)
Cl(3)–Pd(2)–Cl(4)	90.4(7)	C(20)–N(6)–C(22)	106.4(5)
C(16)–N(5)–C(18)	107.2(6)	C(20)–N(6)–Pd(2)	126.8(4)



Scheme 3.

The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of **4** establish that the two mim rings are inequivalent. In the <sup>1</sup>H-NMR spectrum, the Pd–CHCl<sub>2</sub> resonance is identified at  $\delta$  6.34, which is the only singlet in the downfield region. In the <sup>13</sup>C-NMR spectrum, the Pd–CHCl<sub>2</sub> resonance is identified at  $\delta$  62.1, which is the only methine carbon resonance other than the CH(mim)<sub>2</sub>(hexyl) resonance according to DEPT-135 and DEPT-90 NMR experiments. These chemical shifts are close to those of the –CHCl<sub>2</sub> unit of (dpe)Pd(CHCl<sub>2</sub>)Cl (<sup>1</sup>H  $\delta$  5.98; <sup>13</sup>C {<sup>1</sup>H}  $\delta$  72.3) [14]. The positive ion ESI mass spectrum [29] of **4** in CH<sub>2</sub>Cl<sub>2</sub>–MeCN contains peak envelopes with isotope distributions that match calculated patterns for {(hexyl)HC(mim)<sub>2</sub>}Pd(CHCl<sub>2</sub>)<sup>+</sup>, {(hexyl)HC(mim)<sub>2</sub>}Pd(CHCl<sub>2</sub>)(MeCN)<sup>+</sup> and [(hexyl)HC(mim)<sub>2</sub>}Pd(CHCl<sub>2</sub>)<sub>2</sub>( $\mu$ -Cl)<sup>+</sup>, which are expected products of ionization of the Pd–Cl bond of **4** in CH<sub>3</sub>CN. Observed and calculated molecular ion envelopes from ESIMS spectra of **4** are shown in Fig. 2.

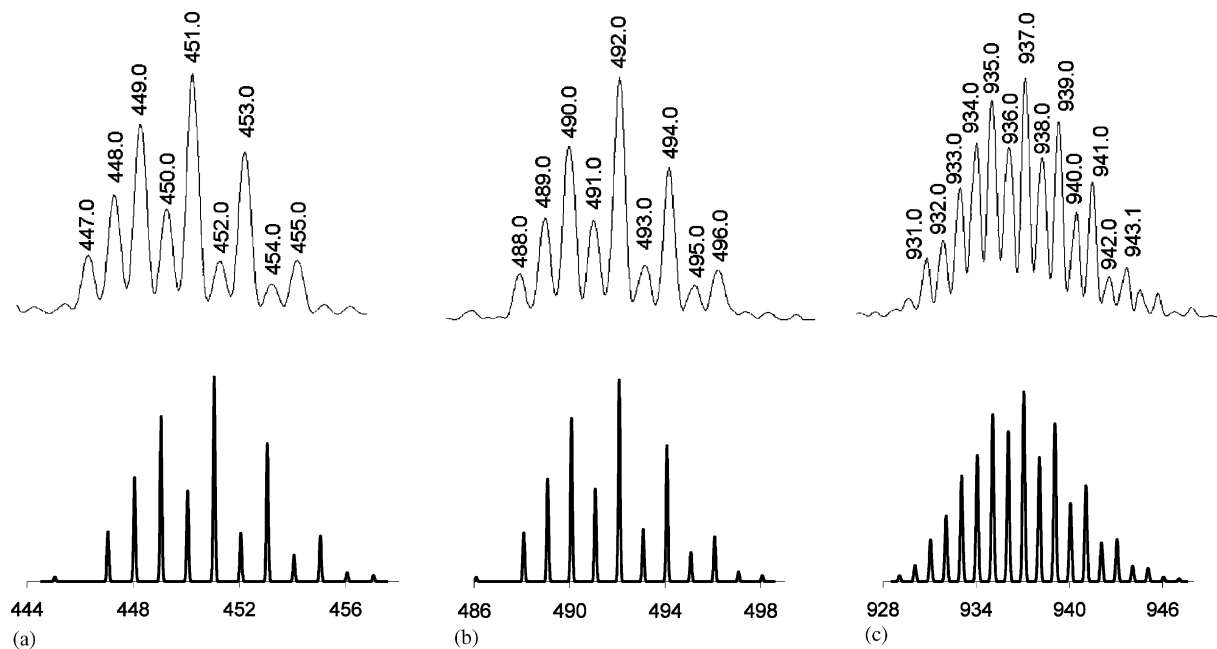


Fig. 2. Observed (top) and calculated (bottom) molecular ion envelopes from ESI mass spectra of cations derived from **4**: (a)  $\{(\text{hexyl})\text{HC}(\text{mim})_2\}\text{Pd}(\text{CHCl}_2)^+$ ; (b)  $\{(\text{hexyl})\text{HC}(\text{mim})_2\}\text{Pd}(\text{CHCl}_2)(\text{MeCN})^+$ ; (c)  $[\{(\text{hexyl})\text{HC}(\text{mim})_2\}\text{Pd}(\text{CHCl}_2)](\mu\text{-Cl})^+$ .

### 2.5. Molecular structure of **4**

The molecular structure of **4** was determined by X-ray diffraction. ORTEP views of **4** are shown in Fig. 3. The crystallographic data and a list of selected bond distances and angles for **4** are given in Tables 1 and 3, respectively.

The core structure of **4** is very similar to that of **2**. The geometry at Pd is square planar, with the sum of the angles at Pd being  $360.1^\circ$ , and the Pd lies  $0.03 \text{ \AA}$  out of the  $\text{N}(1)\text{-N}(2)\text{-C}(1)\text{-Cl}(1)$  plane. The  $\text{N}(1)\text{-Pd-N}(2)$  angle is  $86.4(2)^\circ$ , and the other angles at Pd are close to  $90^\circ$ . The chelate ring adopts a boat conformation which is very similar to that of **2**. The  $\text{N-C-C-N/C-C-C}$  dihedral angle ( $\text{N}(1)\text{-C}(5)\text{-C}(9)\text{-N}(2)/\text{C}(9)\text{-C}(10)\text{-C}(5) = 144.4^\circ$ ) is similar to that in **2**, while the  $\text{N-C-C-N/N-Pd-N}$  dihedral angle ( $\text{N}(1)\text{-C}(5)\text{-C}(9)\text{-N}(2)/\text{N}(1)\text{-Pd-N}(2) = 153.0^\circ$ ) is ca.  $8^\circ$  smaller than the corresponding dihedral angle in **2**. This difference is ascribed to greater steric repulsion between the  $\text{CHCl}_2$  group and the  $(\text{hexyl})\text{HC}(\text{mim})_2$  ligand in **4**, versus the smaller Cl and the  $(\text{hexyl})\text{HC}(\text{mim})_2$  ligand in **2**. The  $\text{Pd}(1)\text{-N}(2)$  bond length ( $2.095(5) \text{ \AA}$ ) is slightly longer than  $\text{Pd}(1)\text{-N}(1)$  bond length ( $2.055(5) \text{ \AA}$ ), which shows that the  $\text{CHCl}_2$  ligand has a higher *trans* influence than chloride. The  $\text{Pd}(1)\text{-C}(1)$  ( $2.035(6) \text{ \AA}$ ) and  $\text{Pd}(1)\text{-Cl}(1)$  ( $2.314(2) \text{ \AA}$ ) distances are both shorter than the corresponding distances in  $(\text{dppe})\text{Pd}(\text{CHCl}_2)\text{Cl}$  ( $\text{Pd-C}$ :  $2.105(5) \text{ \AA}$ ;  $\text{Pd-Cl}$ :  $2.356(1) \text{ \AA}$ ). The two chloride atoms of the  $-\text{CHCl}_2$  unit both point away from the  $\text{Pd-Cl}(1)$  unit, which minimizes steric crowding between those groups. The same orientation of the  $-\text{CHCl}_2$  unit was

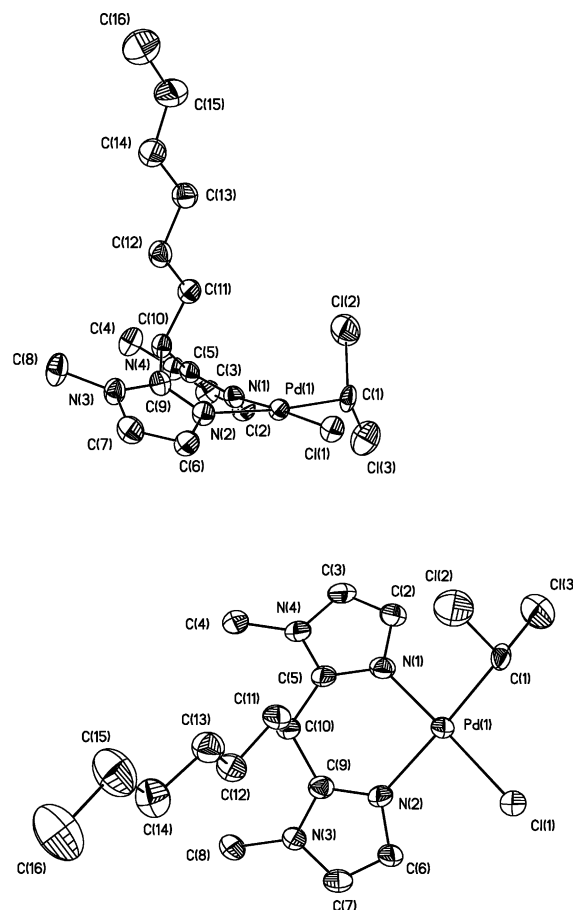


Fig. 3. Two views of the molecular structure of  $\{(\text{hexyl})\text{HC}(\text{mim})_2\}\text{Pd}(\text{CHCl}_2)\text{Cl}$  (**4**). Hydrogen atoms are omitted.

Table 3  
Selected bond lengths (Å) and angles (°) for **4**

Bond lengths			
C(1)–Pd(1)	2.035(6)	C(1)–Cl(2)	1.840(7)
C(1)–Cl(3)	1.665(8)	N(1)–Pd(1)	2.055(5)
N(2)–Pd(1)	2.095(5)	N(1)–C(5)	1.318(8)
N(2)–C(9)	1.323(8)	C(5)–C(10)	1.504(8)
C(9)–C(10)	1.506(8)	Cl(1)–Pd(1)	2.314(2)
Bond angles			
Cl(2)–C(1)–Cl(3)	111.9(4)	Cl(3)–C(1)–Pd(1)	122.7(4)
Cl(2)–C(1)–Pd(1)	105.5(3)	N(1)–C(5)–C(10)	125.4(5)
C(5)–N(1)–Pd(1)	123.5(4)	N(2)–C(9)–C(10)	124.8(5)
C(9)–N(2)–Pd(1)	122.8(4)	N(1)–Pd(1)–N(2)	86.4(2)
C(1)–Pd(1)–Cl(1)	89.3(2)	C(5)–C(10)–C(9)	110.3(5)
N(1)–Pd(1)–C(1)	93.3(2)	N(2)–Pd(1)–Cl(1)	91.1(1)

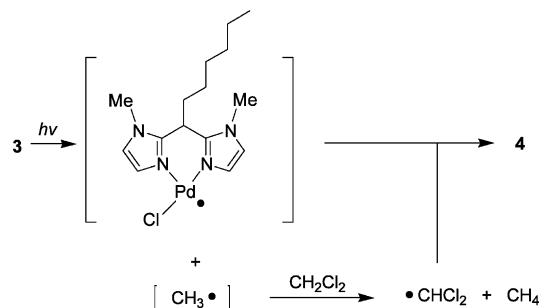
observed in (dppe)Pd(CHCl<sub>2</sub>)Cl [14]. This orientation results in a close H···Cl contact between the Pd–CHCl<sub>2</sub> and Pd–Cl atoms which raises the possibility of CCl<sub>2</sub>H···Cl hydrogen bonding [30]. The possibility of an interaction between the hydrogen of the CHCl<sub>2</sub> group and the chlorine atom on Pd was investigated by <sup>13</sup>C-NMR and IR measurements. For **4**, the –CHCl<sub>2</sub> <sup>13</sup>C resonance appears as a doublet at δ 62.1 with a <sup>1</sup>J<sub>CH</sub> value of 182 Hz. This <sup>1</sup>J<sub>CH</sub> value is similar to values for organic compounds containing CHCl<sub>2</sub> groups, such as 1,1,2,2-tetrachloroethane (180 Hz) [31], and dichloromethane (178 Hz) [32]. The IR spectrum of **4** shows a ν<sub>CH</sub> stretch for the –CHCl<sub>2</sub> group at 2956 cm<sup>-1</sup> (ν<sub>CD</sub> = 2227 cm<sup>-1</sup> for (hexyl)HC(mim)<sub>2</sub>Pd(CDCl<sub>2</sub>)Cl (**4-d**)), which is similar to that for Cl<sub>2</sub>CHCHCl<sub>2</sub> (2985 cm<sup>-1</sup>) [33]. Thus there is no compelling NMR or IR evidence for hydrogen bonding in **4**.

The Pd–CHCl<sub>2</sub> bond distance (2.035(6) Å) is similar to Pd–Me bond distances in related L<sub>2</sub>Pd(Me)Cl complexes, in which the Me group is trans to a neutral N-donor ligand, e.g. (C(=O)(N-methylbenzimidazol-2-yl)<sub>2</sub>)Pd(Me)Cl (2.030(4) Å) [34] and {8-(2-pyridyl)quinoline}Pd(Me)Cl (2.031(5) Å) [35]. The close similarity of Pd–CHCl<sub>2</sub> and Pd–Me distances in those systems reflects a balance of electronic and steric effects. It is well established that M–CF<sub>3</sub> bonds are shorter (typically by 0.05 Å) than corresponding M–Me bonds. This difference has been ascribed to hybridization effects, increased ionic character in M–CF<sub>3</sub> versus M–CH<sub>3</sub> bonds and, more controversially, to d–σ<sub>C–F</sub>\* backbonding [36]. The presence of the two electron withdrawing α-Cl substituents in a Pd–CHCl<sub>2</sub> complex might be expected to shorten the Pd–C bond for the same reasons that M–CF<sub>3</sub> bonds are short. However, due to the large Cl radius, this effect will be attenuated by steric crowding. In fact, in complex **4** there is a close contact between one α-Cl and a mim hydrogen (H(2)–Cl(3): 2.692 Å), which is shorter than the sum of van der Waals radii of H and Cl (2.95 Å) [37], indicative of steric crowding between these ligands.

## 2.6. Reaction mechanism

Compound **3** is stable in CH<sub>2</sub>Cl<sub>2</sub> solution at ambient temperature for days, but only if protected from light. If a CH<sub>2</sub>Cl<sub>2</sub> solution of **3** is exposed to ambient room light in the absence of O<sub>2</sub>, the formation of **4** is observed within 4 h and is complete within 68 h. Previous studies show that photolysis of Pd(II), Pt(II), Pt(IV) and other metal alkyls can result in M–R bond homolysis [38]. Thus, it is likely that the conversion of **3** to **4** involves photolysis of **3** to generate a Pd(I) species and CH<sub>3</sub>•, H atom abstraction from the solvent by CH<sub>3</sub>•, and coupling of the Pd(I) and •CHCl<sub>2</sub> intermediates, as shown in Scheme 4. Consistent with this mechanism, exposure of a solution of **3** in CD<sub>2</sub>Cl<sub>2</sub> to ambient light resulted in the formation of CDH<sub>3</sub> (identified by the characteristic 1:1:1 triplet (*J*<sub>HD</sub> = 2.0 Hz) at δ 0.18 in the <sup>1</sup>H-NMR spectrum, and {(hexyl)HC(mim)<sub>2</sub>}Pd(CDCl<sub>2</sub>)Cl (**4-d**)), which was confirmed by the characteristic Pd(CDCl<sub>2</sub>) resonance (1:1:1 triplet, <sup>1</sup>J<sub>CD</sub> = 29 Hz) at δ 62.1 in the <sup>13</sup>C-NMR spectrum. The mechanism of the conversion of **4** to **2** is unknown at this time.

Similar reactivity for **3** was found in CD<sub>2</sub>ClCD<sub>2</sub>Cl and CDCl<sub>3</sub>. In CD<sub>2</sub>ClCD<sub>2</sub>Cl solution, **3** converts to **2** in the presence of ambient room light over the course of 45 days. No intermediate species, e.g. {(hexyl)HC(mim)<sub>2</sub>}Pd(CDClCD<sub>2</sub>)Cl, were detected although CDH<sub>3</sub> was observed. In this case, it is expected that the methyl radical produced by homolysis of **3** reacts with the solvent to form CDH<sub>3</sub>, while the palladium radical couples with the resulting solvent-derived radical to form {(hexyl)HC(mim)<sub>2</sub>}Pd(CDClCD<sub>2</sub>)Cl. This species was not detected, possibly due to fast β-Cl elimination to form **2** [1e]. The reaction of **3** in CDCl<sub>3</sub> in ambient room light is fast and produces **2** along with CH<sub>4</sub>, CDH<sub>3</sub>, CH<sub>3</sub>CDCl<sub>2</sub>, CH<sub>3</sub>CCl<sub>3</sub>, and CH<sub>3</sub>Cl, which are formed by coupling of radical intermediates [38]. In contrast, **3** decomposes to Pd<sup>0</sup> in C<sub>6</sub>D<sub>5</sub>Cl solution, apparently by a non-photochemical process.



Scheme 4.



### 3. Conclusions

The reaction of  $\{(\text{hexyl})\text{HC}(\text{mim})_2\}\text{Pd}(\text{Me})\text{Cl}$  (**3**) in  $\text{CH}_2\text{Cl}_2$  in ambient room light yields  $\{(\text{hexyl})\text{HC}(\text{mim})_2\}\text{Pd}(\text{CHCl}_2)\text{Cl}$  (**4**). This reaction proceeds by homolysis of the Pd–Me bond of **3**. The molecular structure of **4** has been determined by X-ray diffraction and the Pd–C bond length falls in the range observed for related  $\text{L}_n\text{Pd}(\text{Me})\text{Cl}$  complexes, reflecting a balance of electronic and steric effects.

### 4. Experimental

#### 4.1. Starting materials and general conditions

##### 4.1.1. General comments

All manipulations were performed using dry box or Schlenk techniques under an  $\text{N}_2$  atmosphere, or on a high-vacuum line unless otherwise indicated. Solvents were distilled from appropriate drying/deoxygenating agents (THF: sodium benzophenone ketyl;  $\text{CH}_2\text{Cl}_2$ :  $\text{CaH}_2$ ;  $\text{CDCl}_3$ ,  $\text{CD}_2\text{Cl}_2$ ,  $\text{C}_6\text{D}_5\text{Cl}$ , and  $\text{CD}_2\text{ClCD}_2\text{Cl}$ :  $\text{P}_4\text{O}_{10}$ ). Pentane, hexanes, benzene and toluene were purified by passage through columns of activated alumina and BASF R3-11 oxygen removal catalyst. Nitrogen was purified by passage through columns containing activated molecular sieves and Q-5 oxygen scavenger.  $(\text{cod})\text{Pd}(\text{Me})\text{Cl}$  [39],  $(\text{mim})_2\text{CO}$  [21], and  $(\text{mim})_2\text{CH}_2$  [22] were prepared as described in the literature. All other chemicals were purchased from Aldrich and used without further purification. Elemental analyses were performed by Midwest Microlabs (Indianapolis, IN) and Galbraith Laboratories (Knoxville, TN).

NMR spectra were recorded on Bruker DMX-500 or DRX-400 spectrometers, in Teflon-valved tubes, at 23 °C unless otherwise indicated.  $^1\text{H}$ - and  $^{13}\text{C}$ -chemical shifts are reported versus  $\text{SiMe}_4$  and were determined by reference to residual  $^1\text{H}$ - and  $^{13}\text{C}$ -solvent signals. All coupling constants are reported in Hz. DEPT (Distortionless Enhancement by Polarization Transfer) spectra were acquired and processed using standard Bruker programs.

Electrospray mass spectra were recorded on freshly prepared samples (ca. 1 mg  $\text{ml}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ) using an Agilent 1100 LC-MSD spectrometer incorporating a quadrupole mass filter with a  $m/z$  range of 0–3000. A 5  $\mu\text{l}$  sample was injected by flow injection (MeCN) using an autosampler. Purified nitrogen was used as both the nebulizing and drying gas. Typical instrumental parameters: drying gas temperature 350 °C, nebulizer pressure 35 psi, drying gas flow 12.0  $\text{l min}^{-1}$ , fragmentor voltage 70 V.

#### 4.2. Preparations

##### 4.2.1. $(\text{Hexyl})\text{HC}(\text{mim})_2$ (**1**)

A slurry of  $(\text{mim})_2\text{CH}_2$  (1.51 g, 8.60 mmol) in THF (150 ml) at  $-78$  °C was prepared and  $n\text{-BuLi}$  (2.5 M in hexanes, 3.78 ml, 9.45 mmol) was added over 5 min while the mixture was stirred. A clear deep yellow solution formed. The solution was stirred at  $-78$  °C for 2 h, and 1-iodohexane (2.15 g, 10.1 mmol) was added by syringe. The mixture was allowed to warm to 25 °C over 12 h while stirring was maintained. The volatiles were removed under vacuum and the resulting clear oil was dissolved in  $\text{CH}_2\text{Cl}_2$  (200 ml). The  $\text{CH}_2\text{Cl}_2$  solution was washed with  $\text{H}_2\text{O}$  (300 ml),  $\text{NaHCO}_3$  (300 ml), and brine (300 ml), and finally dried over  $\text{Na}_2\text{SO}_4$ . The  $\text{Na}_2\text{SO}_4$  was filtered off and the volatiles were removed from the filtrate under vacuum to afford a clear oil. The oil was suspended in pentane (50 ml) and the pentane was removed under vacuum to give a yellow–white solid. The solid was extracted with hexanes ( $3 \times 200$  ml). The clear extracts were combined and taken to dryness under vacuum to yield a white, fluffy solid (2.04 g, 92%).  $^1\text{H}$ -NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  6.85 (s, 2H, H4-mim), 6.76 (s, 2H, H5-mim), 4.33 (t,  $J=8$ , 1H, CH), 3.44 (s, 6H,  $\text{NCH}_3$ ), 2.25 (q,  $J=8$ ,  $-\text{CHCH}_2\text{CH}_2-$ ), 1.28 (m, 8H,  $\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.86 (t,  $J=6.5$ , 3H,  $\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  147.1, 127.0, 121.9, 38.9, 33.0, 32.1, 31.7, 29.4, 28.0, 23.0, 14.2. Anal. Calc. for  $\text{C}_{15}\text{H}_{24}\text{N}_4$ : C, 69.19; H, 9.29; N, 21.51. Found: C, 68.88; H, 8.85; N, 21.18%.

##### 4.2.2. $\{(\text{Hexyl})\text{HC}(\text{mim})_2\}\text{PdCl}_2$ (**2**)

A solution of  $(\text{cod})\text{PdCl}_2$  (0.536 g, 1.88 mmol) and  $(\text{mim})_2\text{CH}(\text{hexyl})$  (0.500 g, 1.92 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 ml) was stirred for 12 h at 25 °C. The clear orange solution was concentrated to 25 ml under vacuum and cooled to  $-78$  °C for 4 h, resulting in the precipitation of an orange crystalline solid. The solid was collected by filtration, washed with  $\text{Et}_2\text{O}$  ( $3 \times 30$  ml) and hexanes ( $3 \times 30$  ml) and dried under vacuum yielding an orange powder (0.560 g, 68%).  $^1\text{H}$ -NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.43 (s, 2H, H4-mim), 6.88 (s, 2H, H5-mim), 4.25 (t,  $J=7.5$ , 1H, CH), 3.76 (s, 6H,  $\text{NCH}_3$ ), 2.40 (m, 2H,  $\text{CH}_2$ ), 1.36 (m, 4H,  $\text{CH}_2\text{CH}_2$ ), 1.29 (m, 4H,  $\text{CH}_2\text{CH}_2$ ), 0.87 (t,  $J=7$ , 3H,  $\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  143.5, 128.7, 121.2, 38.1, 34.8, 34.6, 31.9, 29.2, 27.7, 22.9, 14.1. Anal. Calc. for  $\text{C}_{15}\text{H}_{24}\text{Cl}_2\text{N}_4\text{Pd}$ : C, 41.16; H, 5.05; N, 12.80. Found: C, 41.09; H, 5.51; N, 12.55%.

##### 4.2.3. $\{(\text{Hexyl})\text{HC}(\text{mim})_2\}\text{Pd}(\text{Cl})\text{Me}$ (**3**)

A solution of  $(\text{cod})\text{Pd}(\text{Cl})\text{Me}$  (0.40 g, 1.5 mmol) and  $(\text{mim})_2\text{CH}(\text{hexyl})$  (0.41 g, 1.6 mmol) in benzene (30 ml) was stirred for 2 h at 25 °C. A white solid precipitated immediately. The solid was isolated by filtration, rinsed with benzene ( $2 \times 20$  ml), and dried under vacuum (0.60 g, 94%).  $^1\text{H}$ -NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.23 (d,  $J=1$ , 1H, H4/

H5-mim), 6.99 (d,  $J = 1$ , 1H, H4/H5-mim), 6.90 (d,  $J = 1$ , 1H, H4/H5-mim), 6.81 (d,  $J = 1$ , 1H, H4/H5-mim), 4.17 (t,  $J = 7.6$ , 1H, CH), 3.74 (s, 3H, NCH<sub>3</sub>), 3.69 (s, 3H, NCH<sub>3</sub>), 2.43 (m, 1H, CHCH<sub>2</sub>), 2.27 (m, 1H, CHCH<sub>2</sub>), 1.22 (m, 8H, (CH<sub>2</sub>)<sub>4</sub>), 0.85 (t,  $J = 7$ , 3H, CH<sub>2</sub>CH<sub>3</sub>), 0.61 (s, 3H, PdCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  146.0, 144.2, 127.5, 127.4, 121.1, 121.0, 38.1 (CH<sub>2</sub>), 34.5 (NCH<sub>3</sub>), 34.0 (CH), 33.8 (NCH<sub>3</sub>), 31.9, (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 27.7 (CH<sub>2</sub>), 22.8 (CH<sub>2</sub>), 14.1 (CH<sub>2</sub>CH<sub>3</sub>), -6.4 (PdCH<sub>3</sub>). Anal. Calc. for C<sub>16</sub>H<sub>27</sub>ClN<sub>4</sub>Pd: C, 46.05; H, 6.52; N, 13.43. Found: C, 45.81; H, 6.49; N, 13.08%.

#### 4.2.4. *{(Hexyl)HC(mim)}<sub>2</sub>Pd(CHCl<sub>2</sub>)Cl (4)*

A Schlenk flask was charged with {(hexyl)HC(mim)}<sub>2</sub>Pd(Me)Cl (110 mg, 0.264 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (10 ml) was added by cannula transfer. The pale yellow solution was stirred at 23 °C in the presence of ambient room light for 68 h to yield a clear, more intensely yellow solution. The volatiles were removed under vacuum to afford a pale yellow solid (112 mg, 88%). <sup>1</sup>H-NMR spectrum showed that the sample contained ca. 5% {(hexyl)HC(mim)}<sub>2</sub>PdCl<sub>2</sub> (**2**, vide supra). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.82 (d,  $J = 2$ , 1H), 7.23 (d,  $J = 2$ , 1H), 6.96 (d,  $J = 2$ , 1H), 6.82 (d,  $J = 2$ , 1H), 6.34 (s, 1H, PdCHCl<sub>2</sub>), 4.18 (dd,  $J = 9, 7$ , (CH<sub>2</sub>)<sub>4</sub>CH), 3.75 (s, 3H, N-CH<sub>3</sub>), 3.69 (s, 3H, N-CH<sub>3</sub>), 2.68 (m, 1H, CHCHH), 2.31 (m, 1H, CHCHH), 1.36–1.26 (m, 8H, (CH<sub>2</sub>)<sub>4</sub>), 0.86 (t,  $J = 7$ , 3H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  145.2, 144.6, 127.9, 127.8, 121.2, 121.0, 62.1 (PdCHCl<sub>2</sub>), 38.2 (CH<sub>2</sub>), 34.6 (NCH<sub>3</sub>), 34.2 (CH<sub>2</sub>CH), 34.1 (NCH<sub>3</sub>), 31.8 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 27.6 (CH<sub>2</sub>), 22.8 (CH<sub>2</sub>), 14.1 (CH<sub>2</sub>CH<sub>3</sub>). Anal. Calc. for (C<sub>16</sub>H<sub>25</sub>Cl<sub>3</sub>N<sub>4</sub>Pd)<sub>0.95</sub>·(C<sub>15</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>4</sub>Pd)<sub>0.05</sub>: C, 39.60; H, 5.20; N, 11.58. Found: C, 39.43; H, 5.14; N, 11.48%.

#### 4.3. X-ray crystallography

Crystal, data collection and refinement parameters are collected in Table 1, and full details are provided in the Supporting Information. Suitable crystals of **2**·2CH<sub>2</sub>Cl<sub>2</sub> were grown by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub> solution of **2**. The asymmetric unit contains two molecules of **2** which differ only in the orientation of the apical hexyl chain due to rotation around the hexyl-CH(mim)<sub>2</sub> bond. Two CH<sub>2</sub>Cl<sub>2</sub> solvent molecules are present in the asymmetric unit cell; one CH<sub>2</sub>Cl<sub>2</sub> was slightly disordered and the second was highly disordered. Chlorine atom Cl(8) was disordered across two positions (Cl(8a), Cl(8b)). Carbon atoms C(32) and C(18b) could not be refined anisotropically. Residual electron density peaks and holes are localized around the highly disordered CH<sub>2</sub>Cl<sub>2</sub> of solvation. No anomalous bond lengths or angles were observed.

Single crystals of **4** were grown by layering a solution of **4** (80 mg) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 ml) with pentane (0.5 ml)

and slowly cooling the mixture down to -80 °C. Single crystals of **4** were obtained after 3 days.

## 5. Supplementary material

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre, and allocated the deposition numbers CCDC no. 207054 for **2** and 207053 for **4**. 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 <http://www.ccdc.cam.ac.uk>).

## Acknowledgements

We thank Dr Ian Steele and Rory Waterman for assistance with X-ray diffraction analyses and Dr Chang-Jin Qin for assistance with ESIMS experiments. This work was supported by the Edison Polymer Innovation Corporation and the Department of Energy (DE-FG02-00ER15036).

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