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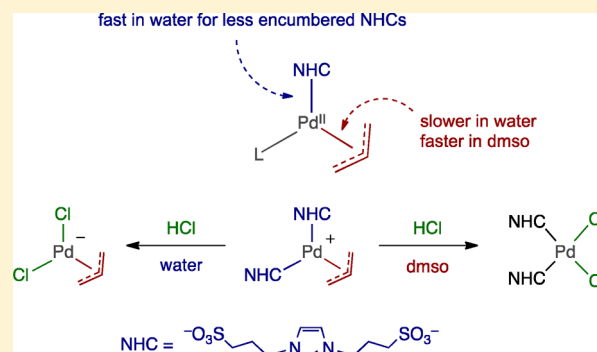
# Aqueous-Phase Chemistry of $\eta^3$ -Allylpalladium(II) Complexes with Sulfonated *N*-Heterocyclic Carbene Ligands: Solvent Effects in the Protolysis of Pd–C Bonds and Suzuki–Miyaura Reactions

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**S** Supporting Information

**ABSTRACT:** The synthesis of water-soluble  $\eta^3$ -allyl Pd(II) complexes containing sulfonated *N*-heterocyclic carbene (NHC) ligands of general formula  $[\text{Pd}(\text{NHC})_n(\eta^3\text{-allyl})\text{Cl}_{2-n}]$  is reported ( $n = 1$  (**1**) or 2 (**8**)). Monocarbene complexes were obtained with the most sterically hindered NHC ligands, and biscarbenes with the less sterically hindered NHCs. The behavior of the isolated complexes in water under acidic, neutral, or alkaline conditions has been studied. The complexes are rather stable in water under neutral or alkaline conditions, although displacement of the chlorido ligand by water or hydroxide occurs under these conditions. In acidic media, Pd–NHC bonds are protolysed, and it is especially noteworthy that this protolysis occurs preferentially to that of the Pd–allyl bonds in the case of the complexes with the less-sterically hindered NHC ligands. This behavior contrasts with that observed in dimethyl sulfoxide (dmsO), where the Pd–allyl bonds are selectively broken upon treatment with Brønsted acids. In addition, Pd–NHC bond breaking was promoted by the addition of a strong  $\sigma$ -donor ligand such as cyanide. Complex **1a** is an active catalyst for the Suzuki–Miyaura cross-coupling of water-soluble aryl chlorides in neat water under moderate conditions (typically, 0.5 mol % Pd and 60 °C).

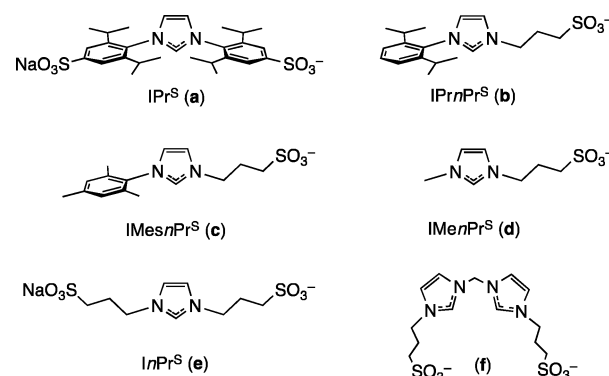


## INTRODUCTION

Water is a unique solvent that is indispensable for biological processes. As such, its use is much sought after by the chemical industry.<sup>1</sup> Catalytic processes in water involving transition metal species are a challenging field that requires a solid understanding of the aqueous chemistry of organometallic compounds.<sup>2</sup> There has been a recent interest in water-soluble transition metal complexes with *N*-heterocyclic carbene (NHC) ligands for applications in aqueous media<sup>3</sup> as a consequence of the important contribution of these ligands in organometallic catalysis.<sup>4</sup> Palladium complexes with hydrophilic NHC ligands, for instance, have been applied for transformations of organic substrates in aqueous media, especially cross-coupling reactions.<sup>5–7</sup> Thus, monocarbene complexes containing the sulfonated ligand IPr<sup>S</sup> (Chart 1) have been shown to generate very active catalytic species for the Suzuki–Miyaura coupling of inactivated and sterically hindered chloroarenes in aqueous media.<sup>5,7</sup>

Although the applications of water-soluble NHC complexes are steadily increasing, there is as yet little information available concerning basic aspects of the chemical reactivity of these complexes in water, including the limits of the hydrolytic stability of metal–NHC bonds. The aim of this work was therefore to gain an understanding of the chemical behavior of water-soluble NHC palladium compounds containing allyl ligands in the aqueous phase.  $[\text{Pd}(\text{NHC})(\eta^3\text{-allyl})\text{Cl}]$  complexes were first reported by Nolan's group in 2002.<sup>8</sup> Upon

## Chart 1. Sulfonated *N*-Heterocyclic Carbenes<sup>a</sup>



<sup>a</sup>For convenience, the NHCs used in this work will always be represented as monoanionic ligands, including those that are dianionic (a and e). The corresponding zwitterionic imidazolium salts will be represented as NHC<sup>S</sup>·H and their sodium salts as NHC<sup>S</sup>·Na.

reduction *in situ*, these complexes generate Pd(0)–NHC species which are very active catalysts for a variety of coupling processes, including the Suzuki–Miyaura and Buchwald–Hartwig reactions.<sup>4a,9</sup> Some of these reactions were first

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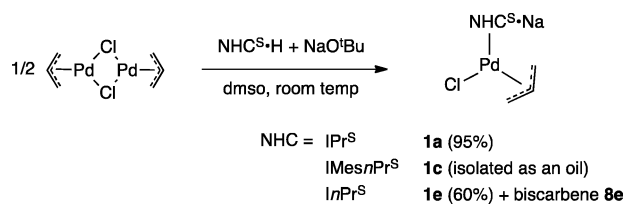
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developed in protic media such as isopropanol, and Plenio's group subsequently showed that the complex  $[\text{Pd}(\text{IPr}^{\text{S}}\text{Na})\text{Cl}(\eta^3\text{-cinnamyl})]$  was very efficient for Suzuki–Miyaura reactions in aqueous media.<sup>5</sup> Here, we report the synthesis of new water-soluble allyl–Pd(II) complexes containing the sulfonated NHC ligands shown in Chart 1, together with studies on their stability and reactivity in water. Whereas these complexes are fairly stable in alkaline or neutral aqueous solutions, concurrence between the protolysis of Pd–carbene and Pd–allyl bonds has been observed in acidic media. In contrast, only protolysis of the Pd–allyl bonds is observed under similar conditions in dimethyl sulfoxide (dmsO). The stability of complex **1a** under alkaline conditions has implications in the possible routes for the activation of this complex in aqueous-phase Suzuki–Miyaura reactions, which are also studied in this report.

## RESULTS AND DISCUSSION

**Monocarbene  $[\text{Pd}(\text{NHC}^{\text{S}}\text{Na})(\text{allyl})\text{Cl}]$ .** Sulfonated monocarbene complexes **1a** and **1c** were obtained following a conventional route involving the reaction of  $[\text{Pd}(\eta^3\text{-allyl})(\mu\text{-Cl})_2]_2$  with free carbene generated *in situ* from the corresponding imidazolium salt and sodium *tert*-butoxide (Scheme 1).<sup>8b–d,10</sup> The preparation was performed in dmsO

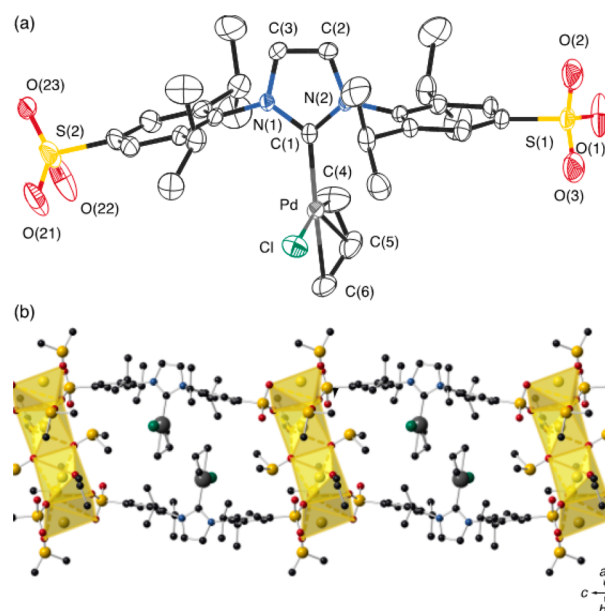
### Scheme 1. Synthesis of Monocarbene Complexes



due to the limited solubility of sulfonated imidazolium salts in solvents such as tetrahydrofuran in which their conventional analogues are usually synthesized. Complex **1a** was isolated from dmsO solution as a white and analytically pure solid in almost quantitative yield (95%) by precipitation with dichloromethane, whereas **1c** was obtained as an oil by lyophilization. This product was soluble in all mixtures of dmsO with miscible solvents tested, and evaporation of the high boiling point solvent by gentle heating under high vacuum always resulted in partial decomposition of the sample. Both complexes are highly soluble and stable in water under aerobic conditions. Attempts to prepare the *InPr*<sup>S</sup> analogue resulted in low selectivities and formation of a mixture of mono (**1e**) and biscarbene complexes (**8e**), in agreement with previous findings in the synthesis of similar complexes with sterically unencumbered NHCs.<sup>11</sup> Formation of the biscarbene complex is assisted by the favorable thermodynamics: a slow but evident increase of the ratio of bis- to monocarbene was observed by <sup>1</sup>H NMR spectroscopy when the reaction mixture was maintained under stirring after consumption of the free carbene.

In the <sup>1</sup>H NMR spectrum, whereas the protons bonded to the central allyl ( $\delta_{\text{C}} = 113.5$  ppm,  $\delta_{\text{H}} = 4.88$  ppm) and to one of the terminal carbons ( $\delta_{\text{C}} = 70.0$  ppm,  $\delta_{\text{H}} = 3.64$  and 2.59 ppm) in **1a** gave sharp resonances in dmsO-*d*<sub>6</sub> at room temperature, those bonded to the second terminal carbon were observed as broad resonances ( $\delta_{\text{C}} = 48.8$  ppm,  $\delta_{\text{H}} = 3.64$  and  $\sim 3.0$  ppm). Broadened resonances were also observed for several isopropyl <sup>1</sup>H (and <sup>13</sup>C) resonances in **1a** and for the corresponding

protons in **1c**. This broadening is a consequence of a  $\eta^3\text{-}\eta^1$  allyl isomerization process that exchanges the *syn* and *anti* protons on the carbon *cis* to the NHC ligand.<sup>12</sup> The crystal structure of **1a** is shown in Figure 1 together with a selection of bond

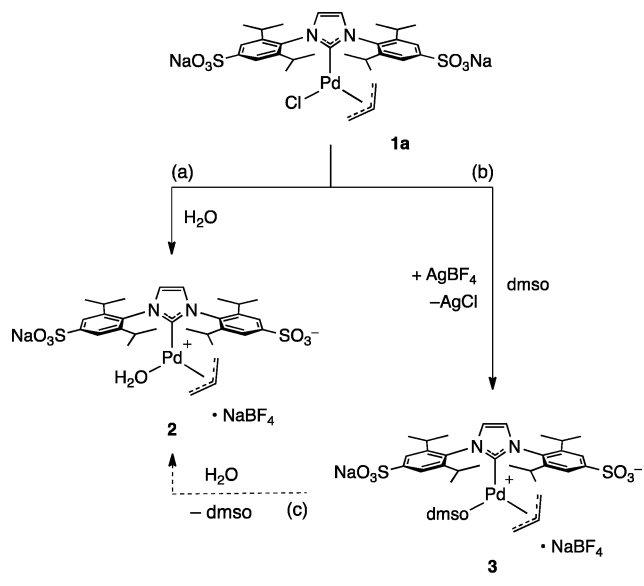


**Figure 1.** (a) ORTEP diagram of the organometallic unit in **1a**.  $2(\text{CH}_3)_2\text{CO} \cdot 3(\text{CH}_3)_2\text{SO}$  (50% probability ellipsoids; H atoms omitted). (b) View along the *c* axis of the double chain of organometallic units showing the coordination environment of the sodium ions as polyhedra (for clarity, acetone molecules occupying the space between the double chains are not shown). Selected bond lengths (Å) and angles (deg): Pd–C(1), 2.046(4); Pd–C(4), 2.115(6); Pd–C(5), 2.133(7); Pd–C(6), 2.205(5); Pd–Cl(1), 2.3748(14); C(1)–N(1), 1.358(5); C(1)–N(2), 1.348(5); N(1)–C(3), 1.398(6); N(2)–C(2), 1.385(6); N(1)–C(7), 1.444(5); N(2)–C(19), 1.453(5); C(1)–Pd–C(4), 99.5(2); C(1)–Pd–C(5), 131.1(3); C(1)–Pd–C(6), 167.7(2); C(4)–Pd–C(6), 68.2(2); C(1)–Pd–Cl, 96.26(12); C(5)–Pd–Cl, 130.4(3); N(2)–C(1)–N(1), 103.5(4).

distances and angles. This complex crystallized with two molecules of acetone and three molecules of dmsO from a mixture of these solvents. The main structural parameters for the organometallic anionic unit (Figure 1a) are essentially coincident with those reported for other  $[\text{Pd}(\text{NHC})(\text{allyl})\text{Cl}]$  complexes and, in particular, for the IPr analogue reported by Nolan and co-workers.<sup>8b</sup> The anionic units are organized in the solid structure in the form of chains via coordination of the sulfonate groups of contiguous units to sodium ions (Figure 1b). The coordination sphere of the sodium ions is completed by acetone and dimethyl sulfoxide molecules (mean Na⋯O distances: 2.493 and 2.37 Å, respectively), two of them bridging sodium ions in contiguous chains to form the double chain represented in Figure 1b.

The <sup>1</sup>H NMR spectrum of **1a** in deuterated water remained unchanged after addition of silver tetrafluoroborate to the aqueous solution. This observation suggested that the chlorido ligand was displaced when this complex was dissolved in water, affording the aqua complex  $[\text{Pd}(\text{IPr}^{\text{S}})(\text{allyl})(\text{OH}_2)]$  (**2**, Scheme 2a). In contrast, dmsO analogue **3** was only obtained when abstraction of the chlorido ligand was forced by addition of  $\text{AgBF}_4$  (Scheme 2b). Complexes **2** and **3** were synthesized as described in the Experimental Section and isolated as

Scheme 2



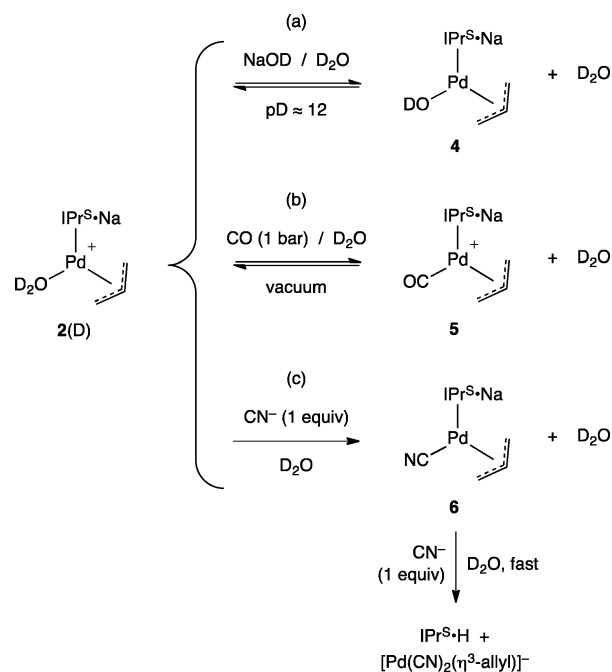
hygroscopic, air-stable, and analytically pure  $\text{NaBF}_4$  addition compounds in moderate yields ( $\sim 60\%$ ). The resonances for the allyl and imidazole ring protons in **3** are shifted to low field in  $\text{dmsO}-d_6$  in respect to the values found in the starting complex **1a** in the same solvent, as expected from the formal positive charge acquired by the metal center (for instance, the central allyl proton resonates at 4.88 ppm in **1a** and at 5.29 ppm in **3**).<sup>13</sup> The presence of a  $\text{dmsO}$  molecule in **3** was supported by elemental analysis, but its coordination to the metal center could not be confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy in  $\text{dmsO}-d_6$  or mass spectrometry. When complex **3** was dissolved in  $\text{D}_2\text{O}$ , the formation of **2** was observed by  $^1\text{H}$  NMR spectroscopy together with a singlet integrating for one molecule at the chemical shift expected for uncoordinated  $\text{dmsO}$  (Figure S7). This result shows that coordination of water competes favorably with that of  $\text{dmsO}$ . In addition, dissociation of the chlorido ligand in **1a** in water but not in  $\text{dmsO}$  might be facilitated by the higher solvation energy of the chloride anion and the higher relative permittivity of water (the respective values are 319 kJ/mol and 80.36 at 20 °C for water and 280 kJ/mol and 47.24 for  $\text{dmsO}$ ).<sup>14</sup>

The use of a stoichiometric amount of silver tetrafluoroborate was found to be important in the synthesis of the above “cationic” complexes in either dimethyl sulfoxide or water. When excesses of the  $\text{Ag}^+$  reagent were used, transmetalation of the NHC ligand from palladium to silver was observed along with the formation of  $(\text{IPr}^S)\text{Ag}^1$  complexes (as expected,<sup>15</sup> a monocarbene was detected by  $^1\text{H}$  NMR spectroscopy in  $\text{dmsO}-d_6$  whereas a biscarbene was formed in  $\text{D}_2\text{O}$ ). In relation with this observation, we note that previous attempts performed by us to obtain water-soluble Pd (or Pt) NHC complexes using silver transmetalating agents in water afforded poor results.

$[\text{Pd}(\text{NHC})(\text{allyl})\text{Cl}]$  complexes catalyze a large number of cross-coupling reactions at low catalyst loadings under mild reaction conditions, often in the presence of an alkaline *tert*-butoxide.<sup>9b</sup> The alkoxide plays the role of a base for the catalyzed reaction while also facilitating the formation of  $[\text{Pd}^0(\text{NHC})]$  active species, with the reductive elimination of allyl *tert*-butyl ether being one of the possible pathways for this formation.<sup>8b,c,e,16</sup> Nevertheless, complex **1a** was recovered without appreciable signs of decomposition after being treated

for several days with an excess of  $\text{NaO}^t\text{Bu}$  at 80 °C in  $\text{dmsO}-d_6$ . As sodium hydroxide is a conventional base for aqueous-phase coupling reactions, we also studied the behavior of **2** in solutions of sodium deuterioxide in deuterated water. The complex is fairly stable under alkaline conditions (only 5% decomposition after 5 days at 45 °C in 0.1 M  $\text{NaOD}$ ), although a substantial shift (between 0.17 and 0.40 ppm to high field) and narrowing of the allyl  $^1\text{H}$  resonances was observed at a pD of around 12, together with a shift of the  $^{13}\text{C}$  carbene carbon resonance 1.5 ppm to low field (Figures S13 and S14). These changes in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum are expected in light of formation of the deuteroxido complex **4** at high pDs (Scheme 3a): The decrease of the formal charge on the

Scheme 3



palladium center displaces the allyl resonances to high field,<sup>13</sup> whereas the increase in the donor ability of the  $\text{X}^-$  ligand slows the allyl dynamics of the  $[\text{Pd}(\text{NHC})(\text{allyl})\text{X}]$  complex.<sup>12</sup> The allyl ligand remains  $\eta^3$ -coordinated in **4**, which contrasts with the formation of the  $\eta^1$ -allyl dimer  $[\text{Pd}(\text{IPr})(\eta^1\text{-cinnamyl})(\mu\text{-OH})]_2$  observed by Egbert et al. when  $[\text{Pd}(\text{IPr})(\eta^3\text{-cinnamyl})\text{Cl}]$  was treated with  $\text{CsOH}$  in THF.<sup>17</sup> Although the  $\eta^1$ -allyl complex is favored in the latter case by the steric hindrance of the cinnamyl ligand, the reduction of the nucleophilicity of the Pd-coordinated hydroxide by the water solvation sphere probably also plays a role in the stabilization of monomeric complex **4**.

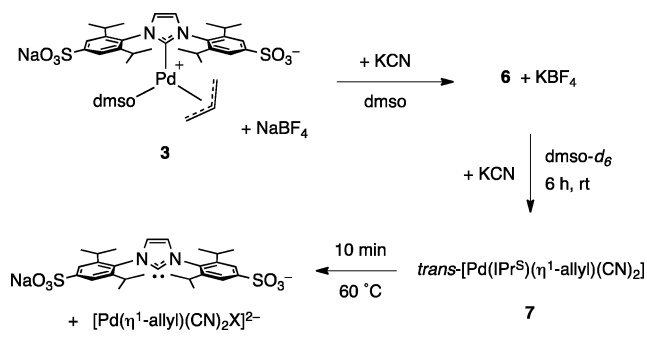
The aqua ligand in **2** was quickly displaced by carbon monoxide under mild conditions (1 bar of CO pressure; Scheme 3b). The reaction was evidenced by the notable shift of the resonances for the central allyl (from 5.05 ppm in **2** to 5.23 ppm in **5**) and imidazole ring protons (from 7.57 to 7.76 ppm). In addition, coordination of the CO ligand to the metal center is apparent by the observation of an intense resonance at 179 ppm in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the reaction mixture when  $^{13}\text{CO}$  was used as reagent. Removal of CO and solvent under vacuum resulted in complete reversion to **2**. Only two other carbonyl Pd–NHC complexes have been reported to



date.<sup>18</sup> Formation of an acyl complex by insertion of the carbonyl ligand into the palladium allyl bond was not observed under these conditions.

The addition of one equivalent of potassium cyanide to a solution of **2** in deuterated water afforded the expected substitution product  $[\text{Pd}(\text{IPr}^{\text{S}})(\eta^3\text{-allyl})(\text{CN})]$  (**6**, Scheme 3c), which was isolated and characterized as a 1:1 mixture with  $\text{KBF}_4$ . Coordination of cyanide was confirmed by observation of a cross-peak at 131.1 ppm in the carbon dimension of the  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum, which was related to the *anti*-allyl proton at 1.65 ppm situated at a distance of three bonds in the molecule.<sup>12</sup> However, the addition of a second equivalent of cyanide rapidly produced decoordination of the NHC ligand and formation of  $[\text{Pd}(\eta^3\text{-allyl})(\text{CN})_2]^-$  (Figure S21).<sup>19</sup> A clearer picture of this decomposition was obtained in dmsO (Scheme 4), where the coordination of a second cyanido ligand

Scheme 4

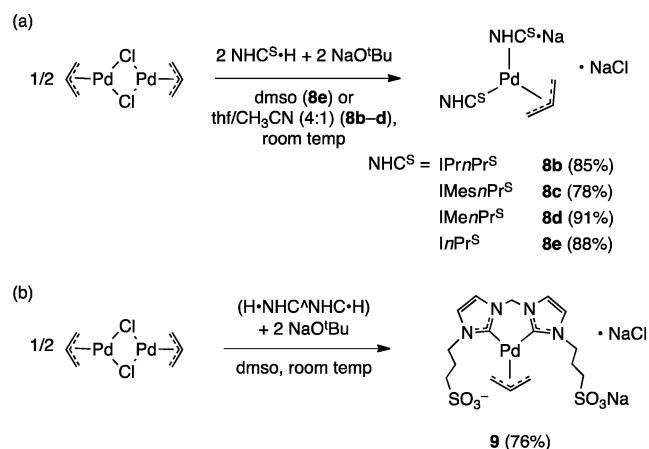


forced the  $\eta^3$  to  $\eta^1$  isomerization of the allyl group to afford **7**. This transformation took 6 h to reach completion at room temperature and was followed by the partial decomposition of **7** into free carbene and  $[\text{Pd}(\eta^1\text{-allyl})(\text{CN})_2\text{X}]^{2-}$  (Figure S22c).<sup>20</sup> Decomposition of the NHC complex **7** was completed by further heating the reaction mixture at 60 °C for 10 min (Figure S22). Grushin and co-workers have reported the formation of very stable  $[\text{Pd}(\text{CN})_3\text{R}]^{2-}$  complexes by displacement of phosphines by cyanide in Pd(II) complexes.<sup>21</sup> However, the fast imidazolium formation in water cannot simply be a result of hydrolysis of the free carbene after displacement of the NHC ligand by cyanide, which is unlikely considering that this displacement takes several hours in dimethyl sulfoxide. In addition, the allyl remains  $\eta^3$ -coordinated to palladium when the process occurs in water. More likely, protonation of the coordinated carbene occurs in concert with the nucleophilic attack of a second cyanide to the palladium center in **6**. The bond polarization induced by this strong  $\sigma$ -donor ligand should provide a lower activation barrier to Pd-carbene protolysis.

Complex **7** was characterized in the reaction mixture by NMR spectroscopy. The  $^{13}\text{C}$  resonances of the carbene carbon and the cyanido ligand were observed at 188.1 and 139.5 ppm, respectively, and  $\eta^1$ -coordination of the allyl ligand was deduced from the single resonance (a doublet) observed at 1.64 ppm, integrating for two hydrogens, and the  $^{13}\text{C}$  chemical shifts at 14.8 (Pd-CH<sub>2</sub>), 99.9, and 147.9 ppm (olefinic carbons, Figure S25). These chemical shifts are very close to those found in  $[\text{Pd}(\eta^1\text{-allyl})(\text{CN})_2\text{X}]^{2-}$  ( $^1\text{H}$ : 1.80 ppm,  $^{13}\text{C}$ : 13.0, 99.7, and 148.2 ppm) and are in sharp contrast with those found in the  $\eta^3$ -allyl complexes.

**Bis-carbenes  $[\text{Pd}(\text{NHC}^{\text{S}})_2(\text{allyl})]^+$ .** Complexes **8b–e** were synthesized by slow addition of sodium *tert*-butoxide to a mixture of the corresponding imidazolium salt and  $[\text{Pd}(\eta^3\text{-allyl})(\mu\text{-Cl})_2]$  (Scheme 5a). The same procedure was used to

Scheme 5. Synthesis of Bis-carbene Complexes



synthesize complex **9**, which bears a methylene-bridged bidentate NHC ligand (Scheme 5b). The fact that the bis-carbene  $[\text{Pd}(\text{IPr}^{\text{S}})_2(\text{allyl})]^+$  could not be obtained is probably due to the hindrance introduced by these sterically demanding NHC ligands. Preparations were initially performed in dimethyl sulfoxide, and the solids were washed with dichloromethane to remove dmsO. Bis-carbenes **8b–d** were isolated in higher yields (78 to 91%) when replacing dmsO with a 4:1 mixture of acetonitrile and tetrahydrofuran, as this procedure avoided further washing with dichloromethane, in which these complexes are partially soluble. The new complexes were characterized by 1D and 2D NMR spectroscopy, mass spectrometry, and elemental analysis. Accurate elemental analyses were obtained for all complexes isolated in their trihydrated form as 1:1 addition compounds with sodium chloride. Attempts to remove the halide salts by dialysis or chromatography resulted in some decomposition of the complexes or in only partial removal of the salt.

The  $^1\text{H}$  NMR spectra of the complexes with asymmetrically substituted NHC ligands (**8b–d**) show the effect of the different steric demand of the ligands on the Pd-carbene rotation rate relative to the NMR time scale, which ranges from slow for the IPrnPr<sup>S</sup> complex **8b** (even at 80 °C in dmsO-*d*<sub>6</sub> or D<sub>2</sub>O, Figure S26) to fast for the IMenPr<sup>S</sup> complex **8d** (at room temperature in dmsO-*d*<sub>6</sub>). The NHC ligands in complex **8b** present an *anti*-conformation that renders the two terminal carbons of the allyl group and the four hydrogens bonded to them inequivalent (Figure 2). In addition, the NHC ligands give two independent sets of  $^1\text{H}$  resonances, with four resonances for the  $\alpha$ -methylene and imidazole ring protons, and eight resonances for the methyl protons of the isopropyl groups. In contrast, the  $^1\text{H}$  NMR spectrum for complex **8d** (and for the symmetrically substituted complex **8e**) shows single resonances for the *syn* and *anti* protons and the terminal carbons of the allyl group. The  $^1\text{H}$  NMR spectrum of complex **8c** at room temperature in dmsO-*d*<sub>6</sub> or D<sub>2</sub>O shows broad resonances for several of the protons involved in exchange as a result of Pd-NHC bond rotation. Free activation energies ( $\Delta G^\ddagger$ ) at the coalescence temperature were calculated using the Eyring equation (Table S1)<sup>22</sup> for the various coalescence

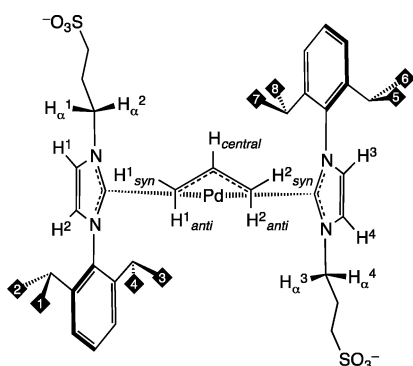


Figure 2. Projection of the *anti* conformation of **8b**.

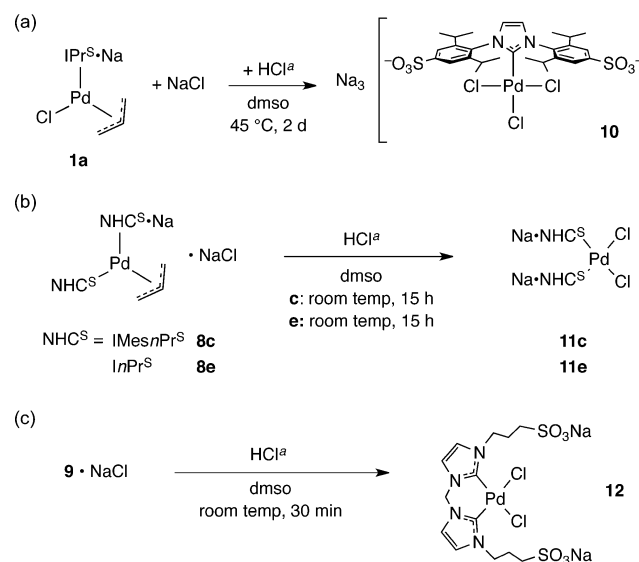
processes observed between 283 and 303 K in the variable-temperature spectra recorded in a mixture of CD<sub>3</sub>CN/dms<sub>o</sub>-d<sub>6</sub> to avoid solvent freezing. An average energy barrier of  $62 \pm 1$  kJ·mol<sup>-1</sup> for Pd–NHC rotation can be estimated from the average of the six  $\Delta G^\ddagger$  values thus determined (ranging from 60.8 to 63.0 kJ mol<sup>-1</sup>). It is important to note that the two halves of the aryl group (*ortho*-methyls and *meta*-hydrogens) are nonequivalent even at high temperatures. This confirms the absence of rotation in the  $\eta^3$ -allyl group which, together with the Pd–NHC rotation, would exchange those protons and make them undistinguishable. It has been reported that the apparent  $\pi$ -rotation of allyl groups around Pd– $\eta^3$ -allyl bonds is generally due to changes in other ligands in the complexes.<sup>23</sup> The characterization of **8c** was completed by <sup>1</sup>H–<sup>13</sup>C HMBC and HSQC NMR spectroscopy at 80 °C (Figures S31–S32) where only one resonance was found for the allylic terminal carbons at  $\delta$  59.6 ppm and for the  $\alpha$ -allylic carbons at  $\delta$  48.0 ppm.

Bis-carbenes **8** and **9** were found to be stable in neutral or alkaline media even under moderate heating. The less stable complexes were those with the less hindered NHC ligands, but even in the case of these complexes (**8d** and **8e**), less than 5% imidazolium salt formation was found in their D<sub>2</sub>O solutions after 24 h at 80 °C at a pD of 14. In parallel to the experiments described above for monocarbene **3**, the addition of an excess of KCN in dms<sub>o</sub>-d<sub>6</sub> to **8c** or **8d** produces the  $\eta^3$  to  $\eta^1$  isomerization of the allyl ligand followed by decoordination of the NHC ligands and formation of [Pd( $\eta^1$ -allyl)(CN)<sub>2</sub>X]<sup>2-</sup> after several hours of reaction at room temperature.

#### Solvent Effects in the Reactions with Brønsted Acids.

We showed recently that trihalide **10** shown in Scheme 6a is a very active catalyst for the Suzuki–Miyaura cross-coupling of aryl chlorides under aqueous conditions.<sup>7</sup> This complex was prepared starting from palladium dichloride and the corresponding imidazolium salt in a procedure that was simple but afforded only moderate yields due to some formation of palladium black and losses during workup. An alternative synthetic procedure might consist in the treatment of **1a** with hydrogen chloride in the presence of NaCl (Scheme 6a).<sup>24</sup> This procedure afforded spectroscopically and analytically pure samples of **10**, with yields that compete favorably with those reported previously (65% compared with 54%; both yields are referred to the whole process starting from PdCl<sub>2</sub>), when hydrogen chloride was added as an ethereal solution to **1a** dissolved in dms<sub>o</sub>. The endurance of the Pd–NHC bond in dms<sub>o</sub> under acidic conditions is demonstrated by the selective protolysis of the allyl–Pd bond even in the presence of an excess of HCl (convenient for accelerating the reaction rate).

#### Scheme 6. Reactions with Hydrogen Chloride in dms<sub>o</sub>



<sup>a</sup>HCl in Et<sub>2</sub>O (4 equiv) in 10 mL of dms<sub>o</sub>. <sup>b</sup>HBF<sub>4</sub> (4 equiv) in 10 mL of dms<sub>o</sub>.

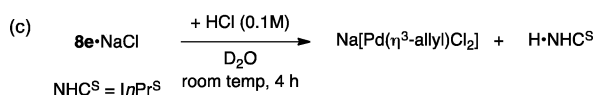
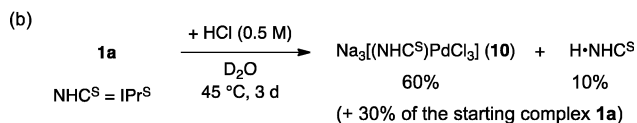
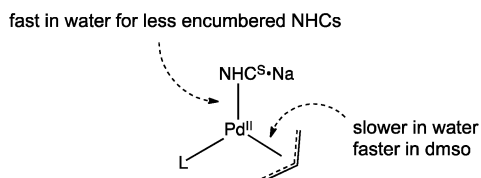
Nevertheless, the dms<sub>o</sub> solvent must be carefully dried as the presence of small amounts of water seems to favor the formation of small amounts of imidazolium salt. Protolysis of the allyl group in bis-carbene complexes **8c,e** and **9** was also selective and faster, especially in the case of chelate complex **9** (Scheme 6b,c). Complex **11c** was isolated in moderate yields (45%) as a yellow, analytically pure solid after workup. The observation of two sets of resonances for the methylene  $\alpha$  to the N in the propylsulfonate chain or for the methyls in the *ortho* position of the mesityl ring implies that the carbene ligands are mutually *cis*, probably adopting an *anti* conformation (no exchange was observed below 80 °C). The usefulness of this route should be noted for the preparation of *cis*-bis-carbenes, in contrast with the *trans* complexes, which are preferentially obtained by other procedures.<sup>25</sup> The transformation of **9** into **12**<sup>26</sup> was very fast under the same conditions.

In contrast with the selective protolysis of Pd–allyl bonds observed in dms<sub>o</sub>, parallel reactions performed in water occurred differently. In this solvent, Pd–allyl protolysis is slower, and in consequence, higher concentrations of HCl must be used in order to achieve a reaction (Scheme 7a). As an example, the transformation of **1a** into **10** reached only 5% after heating for 2 days at 45 °C in a 0.1 M solution of HCl in deuterated water and 60% after 3 days at the same temperature in 0.5 M HCl (Scheme 7b). Concurrent protolysis of Pd–NHC bonds occurred at these high acid concentrations (around 10% in the preceding example). Cleavage of the Pd–NHC bonds was more extensive with less sterically hindered ligands, being selective in the case of the *InPr*<sup>S</sup> complex **8e**. This complex was transformed into a mixture of the allyl complex Na[Pd( $\eta^3$ -allyl)Cl<sub>2</sub>] and the corresponding imidazolium salt within a few hours under relatively mild conditions (room temperature, 0.1 M DCl; see Scheme 7c and Figures S48 and S49). The formation of a mono(NHC)-allyl intermediate, likely [Pd-(*InPr*<sup>S</sup>)( $\eta^3$ -allyl)Cl], was observed at shorter reaction times.

**Suzuki–Miyaura Cross-Coupling Reactions.** Nolan and co-workers found that complexes of type [(NHC)Pd( $\eta^3$ -R-allyl)Cl] were among the most efficient catalysts for the

Scheme 7. Reactions with Hydrogen Chloride in D<sub>2</sub>O

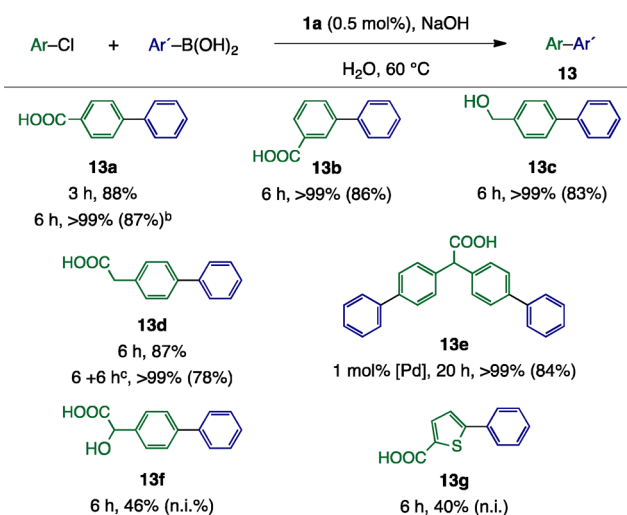
(a) Pd–C bond protolysis



Suzuki–Miyaura cross-coupling of challenging substrates.<sup>8a,b,d,27</sup> Low loadings of these allyl complexes were able to couple unactivated aryl chlorides at room temperature in isopropanol using *tert*-butoxide as the activating base. Plenio and Roy showed that analogous complexes with sulfonated NHC ligands were also useful for the activation of aryl chlorides in aqueous media in the presence of potassium hydroxide.<sup>5</sup> Nevertheless, the coupling temperatures were higher (100 °C) in this case. In addition, *n*-butanol had to be used as cosolvent to increase the solubility of the organic substrates in the aqueous medium. In this context, it has to be mentioned a water-soluble NHC–Pd polymeric complex reported by Karimi and Akhavan that was capable of coupling aryl chlorides at room temperature in neat water with turnover numbers of 1000–2000.<sup>28</sup> In addition, the work of Lipshutz has showed that reactions with water-insoluble substrates can be facilitated at room temperature by the addition of small amounts of surfactants.<sup>29</sup>

The high performance of complexes [Pd(NHC)( $\eta^3$ -R-allyl)Cl] in cross-coupling reactions has been attributed to the facile generation of catalytically active palladium(0) species in the activation step.<sup>8c</sup> Three pathways have been postulated for the reduction of the allyl Pd(II) precursors in the activation step: (a) nucleophilic attack of the base to the  $\eta^3$ -allyl ligand followed by reductive elimination of (Nu)allyl;<sup>30</sup> (b) hydrogen transfer from the  $\alpha$ -carbon of the primary or secondary alcohol commonly used as solvent followed by elimination of (H)allyl;<sup>16a</sup> and (c) transmetalation with the arylboronic acid followed by reductive elimination of (Ar)allyl.<sup>31</sup> We noted above the stability of complex [Pd(IPr<sup>S</sup>·Na)( $\eta^3$ -allyl)Cl] (**1a**) under aqueous basic conditions. Therefore, nucleophilic attack of the hydroxide anion to the allyl ligand cannot be a low-energy profile route for the activation of **1a** in water, and predictably, in other protic solvents. It is well-known that the nucleophilicity of small negatively charged ions is strongly reduced in protic polar solvents by the shell of hydrogen-bonded solvent molecules.<sup>32</sup> The blockage of the nucleophilic-attack route a by the water molecules might be at the origin of the above-referenced observation that cross-coupling reactions require higher temperatures to be developed in aqueous media. We have tested the Suzuki–Miyaura coupling of several aryl chlorides in neat water to gain understanding about the

activation of complex **1a** (Scheme 8). Water is the natural reaction medium for hydrophilic substrates (for instance,

Scheme 8. Synthesis of Biphenyls by Suzuki–Miyaura Cross-Coupling in Water Using Complex **1a** as Catalyst<sup>4c</sup>

<sup>4c</sup>In a typical experiment, a mixture of 0.5 mmol of aryl chloride, 1.2 equiv of arylboronic acid, 3.0 equiv of NaOH, and 0.5 mol % of **1a** were stirred under an argon atmosphere in 2 mL of previously degassed water. <sup>b</sup>Conversion percentages were determined by <sup>1</sup>H NMR integration of the crude product. Percentages in parentheses represent isolated yields after purification; n.i. = not isolated. See the [Experimental Section](#) and [Supporting Information](#) for details. <sup>c</sup>The reaction was stopped after 6 h, charged again with 0.5 mol % of **1a**, and stirred for an additional 6 h period.

carboxylate and other ionic derivatives). The better solubility of these substrates in water adds the potential to circumvent the use of protecting groups. Moreover, the exclusion of primary or secondary alcohols as cosolvents not only impedes the activation of the catalyst through the alcohol reductive pathway b but also prevents the hydrodehalogenation of the aryl chloride by hydrogen transfer from the alcohol. The formation of arenes by ArCl hydrodehalogenation often competes with the cross-coupling reaction, with the consequent reduction of conversions in the desired coupling products, especially for challenging substrates.<sup>7,33</sup>

The catalytic conditions were first optimized for the 4-chlorobenzoic acid substrate (**13a**) starting from the conditions previously reported by our group for the Suzuki–Miyaura cross-coupling of aryl chlorides using trichlorido complex **10** as catalyst (0.5 mol % Pd, 3 equiv of NaOH, 60 °C). The reactions were completed under these conditions in 6 h for the 4- and 3-chlorobenzoic acids and 4-chlorobenzyl alcohol (**13a–c**). Full conversions were also attained for 4-chlorophenylacetic acid (**13d**) when the reaction was prolonged for an additional 6 h period after addition of a second load of catalyst. The double arylation of bis(4-chlorophenyl)acetic acid (**13e**) was completed in the presence of 2 equiv of phenylboronic acid after 20 h of reaction and a catalyst loading of 1.0 mol %. In the case of the carboxylic acid derivatives, the biphenyl products can be isolated by simple filtration after acidification of the solution at the end of the reaction, although we determined isolated yields in all the cases by conventional extraction with an organic solvent. The reactions remained uncompleted under standard conditions for the 2-(4-chlorophenyl)-2-hydroxyacetic (**13f**)



and thiophene-2-carboxylic acids (**13g**). Larger amounts of catalyst or longer reaction times produced the precipitation of high amounts of palladium black, without increasing conversions. No reaction at all was observed for the *ortho*-substituted 2-chlorobenzoic acid. The catalytic activity is likely decreased by chloroarenes able to act as chelating ligands with Pd(II), forming stable five- or six-membered rings (before or after oxidative addition of the Ar–Cl bond).

The above results show that water-soluble [Pd(NHC)( $\eta^3$ -allyl)Cl] complexes are activated for cross-coupling reactions in water under moderate conditions in the absence of an alcohol as cosolvent. Although an exact comparison of activities is not feasible due to the dissimilar nature or solubility of the substrates, the best conditions described for the catalysis of Suzuki couplings by allyl–NHC Pd(II) complexes in organic solvents are softer than those in water (lower temperatures and catalyst loadings). These differences might be reflecting the operation of distinct activation routes: nucleophilic attack of the base to the allyl group versus reduction by the arylboronic acid. Nevertheless, complex [Pd(IPr<sup>S</sup>·Na)( $\eta^3$ -allyl)Cl] (**1a**) operates at temperatures that are significantly lower than those reported for the  $\eta^3$ -cinnamyl analogue by Plenio.<sup>5</sup> Substitution at the terminal position of  $\eta^3$ -allyl ligands has been key for attaining higher catalytic activities with allyl–NHC Pd(II) complexes because this substitution results in a more facile precatalyst activation.<sup>8d</sup> However, the effect of the substitution is expected to depend of the activation route. While the  $\eta^3$ -cinnamyl ligand decreases the energy barrier for the activation step when the nucleophilic-attack route operates,<sup>30</sup> the effect of the increased size of the allyl ligand might be just the opposite for the transmetalation route.

## CONCLUSIONS

Water-soluble  $\eta^3$ -allyl Pd(II) complexes with sulfonated N-heterocyclic ligands have been prepared by reaction of [Pd( $\eta^3$ -allyl)( $\mu$ -Cl)]<sub>2</sub> with the appropriate carbenes generated *in situ*. While sterically hindered NHC ligands afforded exclusively monocarbene complexes, only bis-carbenes could be obtained selectively with the less sterically hindered NHCs. The chlorido ligand in monocarbene complex **1a** dissociates in water, a behavior that has not been observed in dmsO. The complexes were stable in water under neutral or alkaline conditions for days, even under moderate heating. Hydrolysis of NHC ligands was, however, promoted by the addition of a strong  $\sigma$ -donor ligand such as cyanide. Protolysis of Pd–C bonds by addition of Brønsted acids is observed in both solvents employed for the reactions (dmsO and water). Nevertheless, the selectivity changes notably with solvent. Thus, the reactions in dmsO are clean and involve exclusively the Pd–allyl bond under the conditions studied, thereby allowing the use of this route for preparative purposes. In contrast, protolysis of the Pd–allyl and Pd–carbene bonds is competitive in water. The latter is faster for the less sterically hindered NHC ligands and contrasts with the inertness shown by these bonds in an aprotic solvent such as dmsO. Complex **1a** is an active catalyst for the Suzuki–Miyaura coupling of water-soluble aryl chlorides in neat water under moderate conditions (typically, 0.5 mol % Pd and 60 °C). Under these conditions, activation of **1a** likely occurs by transmetalation with the arylboronic acid followed by reductive elimination of (Ar)allyl. It is important to consider in the design of optimized catalysts for aqueous-phase reactions that this route differs from that usually proposed for related catalysts

in conventional organic solvents (nucleophilic attack of the base to the  $\eta^3$ -allyl ligand).

## EXPERIMENTAL SECTION

**Reagents and General Techniques.** Complexes were prepared under an argon atmosphere using standard Schlenk techniques. Unless otherwise stated, reagents were used as received from commercial sources. Solvents (synthesis grade) were deoxygenated and dried before use, as reported elsewhere.<sup>34</sup> Dimethyl sulfoxide (dmsO) was dried by passing the solvent through a column of molecular sieve beads (4 Å, 4–8 mesh). Deionized water (type II quality) was obtained using a Millipore Elix 10 UV Water Purification System. [Pd(allyl)( $\mu$ -Cl)]<sub>2</sub> was prepared following literature methods.<sup>35</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using Mercury VX-300 or UnityPlus-500 spectrometers. Chemical shifts ( $\delta$ , ppm) are quoted relative to SiMe<sub>4</sub> and were measured by internal referencing to the <sup>13</sup>C or residual <sup>1</sup>H resonances of the deuterated solvent (<sup>13</sup>C at 39.0 ppm for dmsO-*d*<sub>6</sub>, <sup>1</sup>H at 2.49 ppm for dmsO-*d*<sub>6</sub> and at 4.69 ppm for D<sub>2</sub>O at room temperature; the formula 5.060 – 0.0122*T* + (2.11 × 10<sup>-5</sup>)*T*<sup>2</sup> was used for D<sub>2</sub>O at other temperatures).<sup>36</sup> Coupling constants (*J*) are given in Hz. When required, 2D <sup>1</sup>H–<sup>13</sup>C HSQC and HMBC experiments were carried out for the unequivocal assignment of <sup>1</sup>H and <sup>13</sup>C resonances. The Analytical Services of the Universidad de Alcalá performed the C, H, N, and S analyses using a LECO CHNS-932 microanalyzer. The ESI mass spectra were recorded by the same services using an Agilent G3250AA LC/MSD TOF Multi mass spectrometer or at the Servicio Interdepartamental de Investigación (SIdI) of the Universidad Autónoma de Madrid using an API QSTAR Pulsar I Hybrid MS-QTOF System.

**Synthesis of Sodium ( $\eta^3$ -Allyl)(1,3-bis(2,6-diisopropyl-4-sulfonatophenyl)imidazol-2-ylidene)chloridopalladate(II) (**1a**).** A solution of sodium 1,3-bis(2,6-diisopropyl-4-sulfonatophenyl)imidazolium<sup>37</sup> (0.312 g, 0.547 mmol) and sodium *tert*-butoxide (0.058 g, 0.601 mmol) in dmsO (10 mL) was stirred for 30 min at room temperature and then added slowly to [Pd(allyl)( $\mu$ -Cl)]<sub>2</sub> (0.100 g, 0.273 mmol). The solution was stirred for 10 min and then poured into dry CH<sub>2</sub>Cl<sub>2</sub> (40 mL). Complex **1a** precipitated as a pale white solid, which was separated by filtration, washed with dichloromethane (2 × 20 mL), and dried under vacuum (0.445 g, 95%). Anal. Calcd (%) for C<sub>30</sub>H<sub>47</sub>ClN<sub>2</sub>Na<sub>2</sub>O<sub>10</sub>PdS<sub>2</sub> (**1a**·4H<sub>2</sub>O): C, 42.51; H, 5.59; N, 3.30; S, 7.56. Found: C, 42.73; H, 5.51; N, 3.16; S, 7.86. <sup>1</sup>H NMR (500 MHz, dmsO-*d*<sub>6</sub>):  $\delta$  7.75 (s, 2H, Imz–H<sup>4,5</sup>), 7.52 (s, 4H, Ar–H<sup>3,5</sup>), 4.88 (m, 1H, allyl CH), 3.64 (d, 1H, allyl-*syn*-CHH, <sup>3</sup>J<sub>HH</sub> = 7.5), 3.00 and 2.77 (broad, 5H, <sup>1</sup>Pr–CH and allyl-*syn*-CHH overlapping), 2.59 (d, 1H, allyl-*anti*-CHH, <sup>3</sup>J<sub>HH</sub> = 13.5), 1.55 (broad, 1H, allyl-*anti*-CHH), 1.26 (d, 12H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.6), 1.08 (broad, 12H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, dmsO-*d*<sub>6</sub>):  $\delta$  83.5 (Imz–C<sup>2</sup>), 148.6 (Ar–C<sup>3</sup>), 144.6 (Ar–C<sup>2,6</sup>), 135.3 (Ar–C<sup>1</sup>), 124.9 (Imz–C<sup>4,5</sup>), 120.2 (Ar–C<sup>3,5</sup>), 113.5 (allyl–CH), 70.0 (allyl–CH<sub>2</sub>), 48.8 (allyl–CH<sub>2</sub>), 27.6 (<sup>1</sup>Pr–CH), 25.3 (broad, CH<sub>3</sub>), 22.0 (CH<sub>3</sub>). ESI-MS (negative ion, MeOH) *m/z* (**1a**: C<sub>30</sub>H<sub>39</sub>ClN<sub>2</sub>Na<sub>2</sub>O<sub>6</sub>PdS<sub>2</sub>): 693.1277 [**1a** – 2Na – Cl]<sup>–</sup> (calcd 693.1284) 100%, 364.0462 [**1a** – 2Na]<sup>2–</sup> (calcd 364.0492) 16%.

**Synthesis of Sodium ( $\eta^3$ -Allyl)chlorido(1-mesityl-3-(sulfonatopropyl)imidazol-2-ylidene)palladate(II) (**1c**).** 1-Mesityl-3-(sulfonatopropyl)imidazolium<sup>25</sup> (0.100 g, 0.324 mmol), [Pd(allyl)( $\mu$ -Cl)]<sub>2</sub> (59.3 mg, 0.162 mmol), and sodium *tert*-butoxide (32.6 mg, 0.356 mmol) were stirred in dmsO-*d*<sub>6</sub> (5 mL) at room temperature for 1 h. The solvent was then removed by lyophilization to afford a dark-brown oil. <sup>1</sup>H NMR (300 MHz, dmsO-*d*<sub>6</sub>):  $\delta$  7.59 (s, 2H, Imz–H<sup>5</sup>), 7.31 (s, 2H, Imz–H<sup>4</sup>), 6.96 (s, 4H, Ar–H<sup>3,5</sup>), 5.01 (m, 1H, allyl–CH), 4.36 (broad, 2H, NCH<sub>2</sub>), 3.79 (d, 1H, allyl-*syn*-CHH, <sup>3</sup>J<sub>HH</sub> = 7.2), 3.12 (broad, 1H, allyl-*syn*-CHH), 2.76 (d, 1H, allyl-*anti*-CHH, <sup>3</sup>J<sub>HH</sub> = 13.9), 2.43 (t, 2H, CH<sub>2</sub>SO<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.2), 2.26 (s, 6H, Ar-*p*-CH<sub>3</sub>), 2.15 (quint, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.2), 2.01 (broad, 6H, Ar-*o*-CH<sub>3</sub>), 1.83 (broad, 1H, allyl-*anti*-CHH). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, 353 K, dmsO-*d*<sub>6</sub>):  $\delta$  179.7 (Imz–C<sup>2</sup>), 138.4 (Ar–C<sup>4</sup>), 136.8 (Ar–C<sup>1</sup>), 135.5 (Ar–C<sup>2,6</sup>), 128.9 (Ar–C<sup>3,5</sup>), 123.1 and 123.0 (Imz–C<sup>4,5</sup>), 114.8 (allyl–CH), 70.7 (allyl–CH<sub>2</sub>), 49.4 (NCH<sub>2</sub>), 49.1 (allyl–



CH<sub>2</sub>), 48.6 (CH<sub>2</sub>SO<sub>3</sub>), 27.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 21.1 (*p*-CH<sub>3</sub>), 18.2 (*o*-CH<sub>3</sub>). ESI-MS (negative ion, MeOH) *m/z* (1c: C<sub>18</sub>H<sub>24</sub>ClN<sub>2</sub>NaO<sub>3</sub>PdS): 489.0242 [1c - Na]<sup>-</sup> (calcd 489.0236) 100%.

**Synthesis of Sodium ( $\eta^3$ -Allyl)(1,3-bis(2,6-diisopropyl-4-sulfonatophenyl)imidazol-2-ylidene)(aquo)palladate(II)—Sodium Tetrafluoroborate (1/1) (2-NaBF<sub>4</sub>).** Silver tetrafluoroborate (50.0 mg, 0.257 mmol) was added to a solution of complex 1a (0.218 g, 0.257 mmol) in H<sub>2</sub>O (5 mL). The formation of a white-gray precipitate was immediately observed. After centrifugation for 20 min at 2500 rpm, the solution was decanted and filtered through kieselguhr. The solvent was then evaporated to dryness under vacuum and washed with dichloromethane (3 × 10 mL) to afford 2 as a pale beige solid (0.195 g, 60%). Anal. Calcd (%) for C<sub>30</sub>H<sub>53</sub>BF<sub>4</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>13</sub>PdS<sub>2</sub> (2-NaBF<sub>4</sub>·6H<sub>2</sub>O): C, 37.81; H, 5.61; N, 2.94; S, 6.73. Found: C, 37.16; H, 5.08; N, 3.22; S, 7.30. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ 7.68 (s, 4H, Ar-H<sup>3,5</sup>), 7.57 (s, 2H, Imz-H<sup>4,5</sup>), 5.05 (broad, 1H, allyl-CH), 3.97 (d, 1H, allyl-*syn*-CHH, <sup>3</sup>J<sub>HH</sub> = 7.3), 3.01 (d, 1H, allyl-*anti*-CHH, <sup>3</sup>J<sub>HH</sub> = 13.0), 2.72 (broad, 5H, <sup>1</sup>Pr-CH and allyl-*syn*-CHH), 1.61 (d, 1H, allyl-*anti*-CHH, <sup>3</sup>J<sub>HH</sub> = 11.6), 1.24 (d, 12H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.5), 1.07 (broad, 12H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, D<sub>2</sub>O): δ 181.3 (Imz-C<sup>2</sup>), 147.3 (Ar), 144.2 (Ar-C<sup>2,6</sup>), 137.3 (Ar), 125.1 (Imz-C<sup>4,5</sup>), 121.3 (Ar-C<sup>3,5</sup>), 117.6 (allyl-CH), 76.0 (allyl-CH<sub>2</sub>), 46.8 (allyl-CH<sub>2</sub>), 29.08 (<sup>1</sup>Pr-CH), 25.2, 24.7, 22.2 (<sup>1</sup>Pr-CH<sub>3</sub>). ESI-MS (negative ion, MeOH) *m/z* (2: C<sub>30</sub>H<sub>41</sub>N<sub>2</sub>NaO<sub>7</sub>PdS<sub>2</sub>): 693.1300 [2 - H<sub>2</sub>O - Na]<sup>-</sup> (calcd 693.1290) 100%.

**Synthesis of Sodium ( $\eta^3$ -Allyl)(1,3-bis(2,6-diisopropyl-4-sulfonatophenyl)imidazol-2-ylidene)(dimethyl sulfoxide)palladate(II)—Sodium Tetrafluoroborate (1/1) (3-NaBF<sub>4</sub>).** Silver tetrafluoroborate (0.100 g, 0.514 mmol) was added to a solution of complex 1a (0.435 g, 0.514 mmol) in dmsO (5 mL). The formation of a dark-gray precipitate was observed, and the suspension was centrifuged for 20 min at 2500 rpm. The solution was decanted, and the solvent was evaporated to dryness under vacuum. The pale white solid thus obtained was washed with dichloromethane (3 × 20 mL) and dried under vacuum (0.301 g, 60%). Anal. Calcd (%) for C<sub>32</sub>H<sub>53</sub>BF<sub>4</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>11</sub>PdS<sub>3</sub> (3-NaBF<sub>4</sub>·4H<sub>2</sub>O): C, 39.33; H, 5.47; N, 2.87; S, 9.84. Found: C, 38.92; H, 5.24; N, 2.76; S, 9.73. <sup>1</sup>H NMR (500 MHz, dmsO-*d*<sub>6</sub>): δ 7.97 (s, 2H, Imz-H<sup>4,5</sup>), 7.60 (s, 4H, Ar-CH), 5.29 (m, 1H, allyl-CH), 4.32 (d, 1H, allyl-*syn*-CHH, <sup>3</sup>J<sub>HH</sub> = 7.4), 3.16 (d, 1H, allyl-*anti*-CHH, <sup>3</sup>J<sub>HH</sub> = 13.5), 2.70 (broad, partially under the solvent signal, <sup>1</sup>Pr-CH), 1.90 (broad, 1H, allyl-*anti*-CHH), 1.28 (d, 12H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.3), 1.10 (broad, 12H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, dmsO-*d*<sub>6</sub>): δ 178.2 (Imz-C<sup>2</sup>), 149.4 (Ar), 144.4 (Ar-C<sup>3,5</sup>), 134.4 (Ar), 125.4 (Imz-C<sup>4,5</sup>), 120.8 (Ar), 120.6 (allyl-CH), 74.2 (allyl-CH<sub>2</sub>, the second CH<sub>2</sub>-allyl was not detected), 27.7 (<sup>1</sup>Pr-CH), 24.8 (broad, <sup>1</sup>Pr-CH<sub>3</sub>), 22.0 (<sup>1</sup>Pr-CH<sub>3</sub>). ESI-MS (negative ion, MeOH) *m/z* (3: C<sub>32</sub>H<sub>45</sub>N<sub>2</sub>NaO<sub>7</sub>PdS<sub>3</sub>): 693.1281 [3 - dmsO - Na]<sup>-</sup> (calcd 693.1290) 100%.

**Characterization Data for 4.** <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ 7.68 (s, 4H, Ar-H<sup>3,5</sup>), 7.54 (s, 2H, Imz-H<sup>4,5</sup>), 4.88 (m, 1H, allyl-CH), 3.59 (d, 1H, allyl-*syn*-CHH, <sup>3</sup>J<sub>HH</sub> = 7.4), 2.80–2.60 (m, 5H, <sup>1</sup>Pr-CH and allyl-*anti*-CHH overlapped), 2.47 (broad, 1H, allyl-*syn*-CHH), 1.32 (d, 1H, allyl-*anti*-CHH, <sup>3</sup>J<sub>HH</sub> = 12.1), 1.25 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.7), 1.24 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.7), 1.09 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.7), 1.04 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.7). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, D<sub>2</sub>O): δ 182.7 (Imz-C<sup>2</sup>), 147.0, 146.7, 144.4, 137.5 (Ar), 124.9 (Imz-C<sup>4,5</sup>), 121.5 (Ar-C<sup>3,5</sup>), 115.6 (allyl-CH), 71.2 (allyl-CH<sub>2</sub>), 45.6 (allyl-CH<sub>2</sub>), 28.9 (<sup>1</sup>Pr-CH), 25.2, 24.6, 22.2 (<sup>1</sup>Pr-CH<sub>3</sub>). ESI-MS (negative ion, MeOH) *m/z* (4: C<sub>30</sub>H<sub>39</sub>DN<sub>2</sub>Na<sub>2</sub>O<sub>7</sub>PdS<sub>2</sub>): 693.1314 [4 - OD - 2Na]<sup>-</sup> (calcd 693.1290) 100%.

**Characterization Data for 5.** <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O): <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O): δ 7.76 (s, 2H, Imz-H<sup>4,5</sup>), 7.69, 7.67 (s, 2H, Ar-H<sup>3,5</sup>), 5.23 (m, 1H, allyl-CH), 4.72 (d, partially under HDO signal, allyl-*syn*-CHH), 3.48 (d, 1H, allyl-*syn*-CHH, <sup>3</sup>J<sub>HH</sub> = 6.9), 3.02 (d, 1H, allyl-*anti*-CHH, <sup>3</sup>J<sub>HH</sub> = 13.8), 2.51 (m, 2H, <sup>1</sup>Pr-CH), 2.38 (d, 1H, allyl-*anti*-CHH, <sup>3</sup>J<sub>HH</sub> = 13.8), 1.10–1.06 (m, 24H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, D<sub>2</sub>O): δ 178.8 (CO), 176.2 (Imz-C<sup>2</sup>), 147.8 (Ar-C<sup>4</sup>), 147.6 and 145.6 (Ar-C<sup>2,6</sup>), 138.2 (Ar-C<sup>1</sup>), 126.4 (Imz-C<sup>4,5</sup>), 124.0 (allyl-CH), 122.4 (broad, Ar-C<sup>3,5</sup>), 73.9 (allyl-

CH<sub>2</sub>), 71.5 (allyl-CH<sub>2</sub>, indirectly observed by 2D), 29.4 (broad, <sup>1</sup>Pr-CH), 24.6, 24.4, and 22.7 (CH<sub>3</sub>). ESI-MS (negative ion, CH<sub>3</sub>CN) *m/z* (5: C<sub>31</sub>H<sub>39</sub>N<sub>2</sub>NaO<sub>7</sub>PdS<sub>2</sub>): 693.1 [5 - CO - Na]<sup>-</sup> (calcd 693.1) 100%.

**Synthesis of Sodium ( $\eta^3$ -Allyl)[1,3-bis(2,6-diisopropyl-4-sulfonatophenyl)imidazol-2-ylidene]cyanidopalladate(II)—Potassium Tetrafluoroborate (1/1) (6-KBF<sub>4</sub>).** A solution of complex 3 (0.200 g, 0.205 mmol) and KCN (13.3 mg, 0.205 mmol) in dmsO (5 mL) was stirred at room temperature for 2 h. The solvent was then evaporated to dryness under vacuum, and the resulting off-white solid was washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and dried under vacuum (0.082 g, 42%). Anal. Calcd (%) for C<sub>31</sub>H<sub>47</sub>BF<sub>4</sub>KN<sub>3</sub>Na<sub>2</sub>O<sub>10</sub>PdS<sub>2</sub> (6-KBF<sub>4</sub>·4H<sub>2</sub>O): C, 38.62; H, 4.91; N, 4.36; S, 6.65. Found: C, 38.33; H, 4.62; N, 4.16; S, 6.86. <sup>1</sup>H NMR (500 MHz, dmsO-*d*<sub>6</sub>): δ 7.87 (s, 2H, Imz-H<sup>4,5</sup>), 7.53 (s, 2H, Ar-H<sup>3,5</sup>), 7.50 (s, 2H, Ar-H<sup>3,5</sup>), 4.76 (m, 1H, allyl-CH), 3.65 (d, 1H, allyl-*syn*-CHH, <sup>3</sup>J<sub>HH</sub> = 7.4), 3.33 (allyl-*syn*-CHH; under the resonance of residual H<sub>2</sub>O, confirmed by 2D NMR), 2.93 (quint, 2H, <sup>1</sup>Pr-CH, <sup>3</sup>J<sub>HH</sub> = 6.8), 2.72 (quint, 2H, <sup>1</sup>Pr-CH, <sup>3</sup>J<sub>HH</sub> = 6.7), 2.16 (d, 1H, allyl-*anti*-CHH, <sup>3</sup>J<sub>HH</sub> = 13.1), 1.65 (d, 1H, allyl-*anti*-CHH, <sup>3</sup>J<sub>HH</sub> = 13.1), 1.29 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.7), 1.22 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.7), 1.16 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.8), 1.04 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.7). <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O): δ 7.63 (s, 2H, Imz-H<sup>4,5</sup>), 7.61 (s, 4H, Ar-H<sup>3,5</sup>), 4.71 (m, allyl-CH; partially under the DHO resonance), 3.75 (d, 1H, allyl-*syn*-CHH, <sup>3</sup>J<sub>HH</sub> = 7.4), 3.38 (d, 1H, allyl-*syn*-CHH, <sup>3</sup>J<sub>HH</sub> = 7.4), 2.81 (quint, 2H, <sup>1</sup>Pr-CH, <sup>3</sup>J<sub>HH</sub> = 6.8), 2.65 (quint, 2H, <sup>1</sup>Pr-CH, <sup>3</sup>J<sub>HH</sub> = 6.7), 2.22 (d, 1H, allyl-*anti*-CHH, <sup>3</sup>J<sub>HH</sub> = 13.1), 1.73 (d, 1H, allyl-*anti*-CHH, <sup>3</sup>J<sub>HH</sub> = 13.1), 1.21 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.7), 1.17 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.7), 1.07 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.8), 0.99 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.7). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, dmsO-*d*<sub>6</sub>): δ 182.1 (Imz-C<sup>2</sup>), 148.8 (Ar-C<sup>4</sup>), 144.8 and 144.5 (Ar-C<sup>2,6</sup>), 135.1 (Ar-C<sup>1</sup>), 131.1 (Pd-CN), 125.1 (Imz-C<sup>4,5</sup>), 120.1 and 119.9 (Ar-C<sup>3,5</sup>), 116.4 (allyl-CH), 59.8 (allyl-CH<sub>2</sub>), 57.1 (allyl-CH<sub>2</sub>), 27.3 (broad, <sup>1</sup>Pr-CH), 25.3, 24.6, and 21.7 (CH<sub>3</sub>). ESI-MS (negative ion, MeOH) *m/z* (6: C<sub>31</sub>H<sub>39</sub>N<sub>3</sub>Na<sub>2</sub>O<sub>6</sub>PdS<sub>2</sub>): 742.1221 [6 - Na]<sup>-</sup> (calcd 742.1218) 17%, 359.5690 [6 - 2Na]<sup>2-</sup> (calcd 359.5663) 100%.

**Synthesis of Sodium ( $\eta^3$ -Allyl)bis[1-(2,6-diisopropylphenyl)-3-(sulfonatopropyl)imidazol-2-ylidene]palladate(II)—Sodium Chloride (1/1) (8b-NaCl).** 1-(2,6-Diisopropylphenyl)-3-(sulfonatopropyl)imidazolium<sup>25</sup> (0.382 g, 1.09 mmol), [Pd(allyl)(μ-Cl)]<sub>2</sub> (0.100 g, 0.273 mmol), and sodium *tert*-butoxide (0.125 g, 1.31 mmol) were stirred at room temperature in a mixture of acetonitrile (10 mL) and tetrahydrofuran (40 mL) for 15 h. The solvents were then evaporated under vacuum to dryness. The residue thus obtained was dried under vacuum to afford 8b as an off-white solid (0.455 g, 85%). Anal. Calcd (%) for C<sub>39</sub>H<sub>61</sub>ClN<sub>4</sub>Na<sub>2</sub>O<sub>3</sub>PdS<sub>2</sub> (8b-NaCl·3H<sub>2</sub>O): C, 47.71; H, 6.26; N, 5.71; S, 6.53. Found: C, 47.60; H, 6.42; N, 5.99; S, 6.42. <sup>1</sup>H NMR (300 MHz, dmsO-*d*<sub>6</sub>): δ 7.67 (d, 1H, Imz-H<sup>4,5</sup>, <sup>3</sup>J<sub>HH</sub> = 1.5), 7.64 (s, 2H, Imz-H<sup>4,5</sup>), 7.61 (d, 1H, Imz-H<sup>4,5</sup>, <sup>3</sup>J<sub>HH</sub> = 1.5), 7.54 (t, 1H, Ar-H<sup>4</sup>, <sup>3</sup>J<sub>HH</sub> = 7.8), 7.49 (t, 1H, Ar-H<sup>4</sup>, <sup>3</sup>J<sub>HH</sub> = 7.8), 7.37 (d, 1H, Ar-H<sup>3,5</sup>, <sup>3</sup>J<sub>HH</sub> = 7.8), 7.36 (d, 1H, Ar-H<sup>3,5</sup>, <sup>3</sup>J<sub>HH</sub> = 7.8), 7.31 (d, 1H, Ar-H<sup>3,5</sup>, <sup>3</sup>J<sub>HH</sub> = 7.8), 7.29 (d, 1H, Ar-H<sup>3,5</sup>, <sup>3</sup>J<sub>HH</sub> = 7.8), 5.25 (m, 1H, allyl-CH), 3.68 (d, 1H, allyl-*syn*-CHH, <sup>3</sup>J<sub>HH</sub> = 6.5), 3.61 (d, 1H, allyl-*syn*-CHH, <sup>3</sup>J<sub>HH</sub> = 6.5), 3.00 (m, 2H, NCH<sub>2</sub>), 2.83 (m, 1H, NCH<sub>2</sub>), 2.74 (m, 1H, NCH<sub>2</sub>), 2.57 and 2.54 (overlapped m, 3H, <sup>1</sup>Pr-CH and allyl *anti*-CHH), 2.31 (d, 1H, allyl-*anti*-CHH, <sup>3</sup>J<sub>HH</sub> = 12.7), 2.23 (m, 2H, CH<sub>2</sub>SO<sub>3</sub>), 2.02 (m, 4H, CH<sub>2</sub>SO<sub>3</sub> and <sup>1</sup>Pr-CH overlapping), 1.95 (m, 1H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.83 (m, 1H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.71 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.21 (d, 3H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.7), 1.19 (d, 3H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.7), 1.03 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.6), 0.94 (d, 3H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.7), 0.90 (t, 3H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.7), 0.75 (d, 3H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.4), 0.72 (d, 3H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.8). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, dmsO-*d*<sub>6</sub>): δ 176.2 (broad, Imz-C<sup>2</sup>), 145.6, 145.5, 144.5, and 144.3 (Ar-C<sup>2,5</sup>), 134.8 and 134.5 (Ar-C<sup>1</sup>), 129.5 and 126.4 (Ar-C<sup>4</sup>), 129.4 and 126.2 (Imz-C<sup>5,5'</sup>), 123.6, 123.5, 123.1, and 123.0 (Ar-C<sup>2,6</sup>), 120.1 and 120.0 (Imz-C<sup>4,4'</sup>, not observed in <sup>13</sup>C NMR spectrum, indirectly determined by <sup>1</sup>H-<sup>13</sup>C HMBC), 119.1 (allyl-CH), 60.3 and 59.7 (allyl-CH<sub>2</sub>), 48.2 and 47.9 (NCH<sub>2</sub>), 47.6 and 47.5 (CH<sub>2</sub>SO<sub>3</sub>), 27.3, 27.2, 27.1, 27.0 (<sup>1</sup>Pr-CH), 25.5 and 25.0 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 26.1, 26.0, 25.5, 25.2, 21.2, 20.9, 20.8, and 20.6

(CH<sub>3</sub>). ESI-MS (negative ion, MeOH) *m/z* (8b: C<sub>39</sub>H<sub>55</sub>N<sub>4</sub>NaO<sub>6</sub>PdS<sub>2</sub>): 845.2607 [8b - Na]<sup>-</sup> (calcd 845.2603) 100%.

**Synthesis of Sodium ( $\eta^3$ -Allyl)bis[1-mesityl-3-(sulfonatopropyl)imidazol-2-ylidene]palladate(II)—Sodium Chloride (1/1) (8c-NaCl).** Imidazolium salt 1c (0.337 g, 1.09 mmol), [Pd(allyl)( $\mu$ -Cl)]<sub>2</sub> (0.100 g, 0.273 mmol), and sodium *tert*-butoxide (0.125 g, 1.31 mmol) were stirred at room temperature in a mixture of acetonitrile (10 mL) and tetrahydrofuran (40 mL) for 15 h. The solvents were then evaporated under vacuum to dryness. The residue thus obtained was dried under vacuum to afford 8c as an off-white solid (0.382 g, 78%). Anal. Calcd (%) for C<sub>33</sub>H<sub>49</sub>ClN<sub>4</sub>Na<sub>2</sub>O<sub>9</sub>PdS<sub>2</sub> (8c-NaCl·3H<sub>2</sub>O): C, 44.15; H, 5.50; N, 6.24; S, 7.14. Found: C, 43.84; H, 5.27; N, 6.43; S, 6.81. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O):  $\delta$  7.33 (broad, 2H, Imz-H<sup>4,5</sup>), 6.95 (broad, 4H, Ar-H<sup>3</sup>), 6.93 (s, 2H, Imz-H<sup>4,5</sup>), 5.09 (m, 1H, allyl-CH), 3.75 (d, 2H, allyl-*syn*-CHH, <sup>3</sup>J<sub>HH</sub> = 7.0), 3.40 (broad, 1H, NCH<sub>2</sub>), 3.05 (broad, 2H, NCH<sub>2</sub>), 2.54 (broad, 4H, CH<sub>2</sub>SO<sub>3</sub>), 2.41 (broad, 1H, NCH<sub>2</sub>), 2.22 (s, 6H, Ar-*p*-CH<sub>3</sub>), 1.86 (broad, 6H, allyl-*anti*-CHH and CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, overlapping), 1.74 (broad, 6H, Ar-*o*-CH<sub>3</sub> and), 1.44 (broad, 6H, Ar-*o*-CH<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, dmsO-d<sub>6</sub>):  $\delta$  7.65 (broad, 2H, Imz-H<sup>5</sup>), 7.39 (d, 2H, Imz-H<sup>4</sup>, <sup>3</sup>J<sub>HH</sub> = 1.6), 7.02 (broad, 4H, Ar-H<sup>3</sup>), 5.20 (m, 1H, allyl-CH), 3.79 (broad, 1H, allyl-*syn*-CHH), 3.64 (broad, 1H, allyl-*syn*-CHH), 3.35 (NCH<sub>2</sub>; 1H under the resonance of H<sub>2</sub>O, confirmed by 2D NMR), 3.03 (broad, 2H, NCH<sub>2</sub>), 2.63 (broad, 1H, NCH<sub>2</sub>), 2.50 (allyl-*syn*-CHH; 1H under the resonance of dmsO, confirmed by 2D NMR), 2.30 (s, 7H, Ar-*p*-CH<sub>3</sub> and allyl-*anti*-CHH), 2.10 (broad, 4H, CH<sub>2</sub>SO<sub>3</sub>), 1.81 (broad, 10H, Ar-*o*-CH<sub>3</sub> and CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> overlapping), 1.51 (broad, 6H, Ar-*o*-CH<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, 353 K, dmsO-d<sub>6</sub>):  $\delta$  7.61 (d, 2H, Imz-H<sup>5</sup>, <sup>3</sup>J<sub>HH</sub> = 1.6), 7.32 (d, 2H, Imz-H<sup>4</sup>, <sup>3</sup>J<sub>HH</sub> = 1.6), 7.03 and 7.02 (s, 4H, Ar-*m*-CH), 5.23 (m, 1H, allyl-CH), 3.75 (broad, 2H, allyl-*syn*-CHH), 3.13 (broad, 4H, NCH<sub>2</sub>), 2.39 (broad, 2H, *anti*-allyl CHH), 2.32 (s, 6H, Ar-*p*-CH<sub>3</sub>), 2.22 (broad, 4H, CH<sub>2</sub>SO<sub>3</sub>), 1.85 (broad, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.70 (broad, 12H, Ar-*o*-CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, 353 K, dmsO-d<sub>6</sub>):  $\delta$  175.8 (observed by 2D NMR, Imz-C<sup>2</sup>), 137.6 (Ar-C<sup>2,6</sup>), 134.3 (Ar-C<sup>1</sup>), 128.3 (Ar-C<sup>3,5</sup>), 124.0 (Ar-*o*-Me), 123.4 (Imz-C<sup>5</sup>), 121.1 (Imz-C<sup>4</sup>), 118.4 (allyl-CH), 59.6 (allyl-CH<sub>2</sub>), 48.0 (NCH<sub>2</sub>), 47.1 (CH<sub>2</sub>SO<sub>3</sub>), 25.2 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 19.2 (Ar-*p*-CH<sub>3</sub>), 15.7 (Ar-*o*-CH<sub>3</sub>). ESI-MS (negative ion, MeOH) *m/z* (8c: C<sub>33</sub>H<sub>43</sub>N<sub>4</sub>NaO<sub>6</sub>PdS<sub>2</sub>): 761.1668 [8c - Na]<sup>-</sup> (calcd 761.1664) 100%.

**Synthesis of Sodium ( $\eta^3$ -Allyl)bis(1-methyl-3-(sulfonatopropyl)imidazol-2-ylidene)palladate(II)—Sodium Chloride (1/1) (8d-NaCl).** Sodium *tert*-butoxide (0.125 g, 1.31 mmol) was slowly added to a solution of 1-methyl-3-(sulfonatopropyl)imidazolium<sup>38</sup> (0.223 g, 1.09 mmol) and [Pd(allyl)( $\mu$ -Cl)]<sub>2</sub> (0.100 g, 0.273 mmol) in a mixture of CH<sub>3</sub>CN (10 mL) and THF (40 mL). The resulting suspension was stirred at room temperature for 15 h. The solvents were then removed and the off-white solid thus obtained was dried under vacuum (0.342 g, 91%). Anal. Calcd (%) for C<sub>17</sub>H<sub>33</sub>ClN<sub>4</sub>Na<sub>2</sub>O<sub>9</sub>PdS<sub>2</sub> (8d-NaCl·3H<sub>2</sub>O): C, 29.62; H, 4.82; N, 8.13; S, 9.30. Found: C, 29.23; H, 4.95; N, 7.91; S, 9.75. <sup>1</sup>H NMR (300 MHz, dmsO-d<sub>6</sub>):  $\delta$  7.41 (s, 2H, Imz-H<sup>4,5</sup>), 7.39 (s, 2H, Imz-H<sup>4,5</sup>), 5.50 (m, 1H, allyl-CH), 3.96 (m, 4H, NCH<sub>2</sub>), 3.84 (d, 2H, allyl-*syn*-CHH, <sup>3</sup>J<sub>HH</sub> = 7.2), 3.64 (s, 6H, NCH<sub>3</sub>), 2.77 (d, 2H, allyl-*anti*-CHH, <sup>3</sup>J<sub>HH</sub> = 13.2), 2.33 (t, 4H, CH<sub>2</sub>SO<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.5), 1.88 (t, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.5). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, dmsO-d<sub>6</sub>):  $\delta$  174.7 (Imz-C<sup>2</sup>), 123.0 and 121.7 (Imz-C<sup>4,5</sup>), 118.7 (allyl-CH), 58.9 (allyl-CH<sub>2</sub>), 48.5 (NCH<sub>2</sub>), 47.3 (CH<sub>2</sub>SO<sub>3</sub>), 37.2 (N-CH<sub>3</sub>), 26.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). ESI-MS (negative ion, MeOH) *m/z* (8d: C<sub>17</sub>H<sub>27</sub>N<sub>4</sub>NaO<sub>6</sub>PdS<sub>2</sub>): 553.0416 [8d - Na]<sup>-</sup> (calcd 553.0412) 100%.

**Synthesis of Trisodium ( $\eta^3$ -Allyl)bis(1,3-bis(sulfonatopropyl)imidazol-2-ylidene)palladate(II)—Sodium Chloride (1/1) (8e-NaCl).** A solution of sodium *tert*-butoxide (0.125 g, 1.310 mmol) in dmsO (5 mL) was slowly added, under stirring, to a mixture of sodium 1,3-bis(sulfonatopropyl)imidazolium<sup>39</sup> (0.365 g, 1.092 mmol) and [Pd(allyl)( $\mu$ -Cl)]<sub>2</sub> (0.100 g, 0.273 mmol). The mixture was stirred at room temperature for 30 min, and the solution was evaporated to dryness. The white solid thus obtained was washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and dried under vacuum (0.456 g, 88%). Anal. Calcd (%) for C<sub>21</sub>H<sub>39</sub>ClN<sub>4</sub>Na<sub>4</sub>O<sub>15</sub>PdS<sub>4</sub> (8e-NaCl·3H<sub>2</sub>O): C,

26.56; H, 4.14; N, 5.90; S, 13.50. Found: C, 26.23; H, 4.24; N, 5.71; S, 13.85. <sup>1</sup>H NMR (300 MHz, dmsO-d<sub>6</sub>):  $\delta$  7.43 (s, 4H, Imz-H<sup>4,5</sup>), 5.57 (m, 1H, allyl-CH), 4.04 (broad, 8H, NCH<sub>2</sub>), 3.78 (d, 2H, allyl-*syn*-CHH, <sup>3</sup>J<sub>HH</sub> = 7.5), 2.76 (d, 2H, allyl-*anti*-CHH, <sup>3</sup>J<sub>HH</sub> = 13.3), 2.41 (t, 8H, CH<sub>2</sub>SO<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.5), 1.92 (t, 8H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.5). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, dmsO-d<sub>6</sub>):  $\delta$  174.4 (Imz-C<sup>2</sup>), 121.7 (Imz-C<sup>4,5</sup>), 119.2 (allyl-CH), 59.5 (allyl-CH<sub>2</sub>), 48.7 (NCH<sub>2</sub>), 47.4 (CH<sub>2</sub>SO<sub>3</sub>), 26.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). ESI-MS (negative ion, MeOH) *m/z* (8e: C<sub>21</sub>H<sub>33</sub>N<sub>4</sub>Na<sub>3</sub>O<sub>12</sub>PdS<sub>4</sub>): 812.9822 [8e - Na]<sup>-</sup> (calcd 812.9814) 57%, 394.9982 [8e - 2Na]<sup>2-</sup> (calcd 394.9961) 100%, 255.6687 [8e - 3Na]<sup>3-</sup> (calcd 255.6676) 29%.

**Synthesis of Sodium ( $\eta^3$ -Allyl)(1,1'-bis(sulfonatopropyl)-3,3'-methylenediimidazole-2,2'-diylidene)palladate(II)—Sodium Chloride (1/1) (9-NaCl).** A solution of sodium *tert*-butoxide (0.125 g, 1.31 mmol) in dmsO (5 mL) was slowly added, with stirring, to a mixture of 1,1'-bis(3-sulfonatopropyl)-3,3'-methylenediimidazolium<sup>40</sup> (0.214 g, 0.546 mmol) and [Pd(allyl)( $\mu$ -Cl)]<sub>2</sub> (0.100 g, 0.273 mmol). The mixture was then stirred at room temperature for 30 min and the solvent subsequently removed in vacuum at 80 °C. The resulting off-white solid was washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and dried under vacuum (0.280 g, 76%). Anal. Calcd (%) for C<sub>16</sub>H<sub>29</sub>ClN<sub>4</sub>Na<sub>2</sub>O<sub>9</sub>PdS<sub>2</sub> (9-NaCl·3H<sub>2</sub>O): C, 28.54; H, 4.34; N, 8.32; S, 9.52. Found: C, 28.44; H, 4.24; N, 8.18; S, 9.67. <sup>1</sup>H NMR (300 MHz, dmsO-d<sub>6</sub>):  $\delta$  7.65 (d, 2H, Imz-H<sup>4</sup>, <sup>3</sup>J<sub>HH</sub> = 1.6), 7.53 (d, 2H, Imz-H<sup>5</sup>, <sup>3</sup>J<sub>HH</sub> = 1.6), 6.27 (d, 1H, NCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 13.0), 6.03 (d, 1H, NCH<sub>2</sub>N, <sup>2</sup>J<sub>HH</sub> = 13.0), 5.37 (m, 1H, allyl-CH), 4.19 (broad, 6H, NCH<sub>2</sub>C and allyl-*syn*-CHH overlapping), 2.95 (d, 2H, allyl-*anti*-CHH, <sup>3</sup>J<sub>HH</sub> = 13.4), 2.42 (t, 4H, CH<sub>2</sub>SO<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.5), 1.99 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.5). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, dmsO-d<sub>6</sub>):  $\delta$  174.6 (Imz-C<sup>2</sup>), 122.5 (Imz-C<sup>4</sup>), 121.8 (Imz-C<sup>5</sup>), 119.9 (allyl-CH), 62.7 (NCH<sub>2</sub>N), 59.6 (allyl-CH<sub>2</sub>), 50.3 (NCH<sub>2</sub>), 48.4 (CH<sub>2</sub>SO<sub>3</sub>), 27.9 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). ESI-MS (negative ion, MeOH) *m/z* (9: C<sub>16</sub>H<sub>23</sub>N<sub>4</sub>NaO<sub>6</sub>PdS<sub>2</sub>): 594.9694 [9 + Cl]<sup>-</sup> (calcd 594.9686) 7%, 537.0106 [9 - Na]<sup>-</sup> (calcd 537.0099) 100%.

**Synthesis of Trisodium (1,3-Bis(2,6-diisopropyl-4-sulfonatophenyl)imidazol-2-ylidene)trichloridopalladium(II) (10).** A 0.16 M solution of hydrogen chloride in diethyl ether (14.8 mL, 2.37 mmol) was added to a mixture of 1a (0.500 g, 0.590 mmol) and sodium chloride (34.5 mg, 0.590 mmol) in dmsO (10 mL). The resultant solution was then stirred at 45 °C for 48 h, and the solvent evaporated to dryness under vacuum. The resulting residue was washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and dried under vacuum to give 10 as a yellow solid (0.375 g, 71%). Anal. Calcd (%) for C<sub>27</sub>H<sub>38</sub>Cl<sub>3</sub>N<sub>2</sub>Na<sub>3</sub>O<sub>8</sub>PdS<sub>2</sub> (10·2H<sub>2</sub>O): C, 37.51; H, 4.43; N, 3.24; S, 7.42. Found: C, 37.74; H, 4.75; N, 2.91; S, 7.50. Other characterization data as reported previously.<sup>7</sup>

**Synthesis of Disodium *cis*-Bis(1-mesityl-3-(sulfonatopropyl)imidazol-2-ylidene)dichloridopalladium(II) (11c).** A 0.16 M solution of HCl in diethyl ether (14.0 mL, 2.24 mmol) was added dropwise to a solution of 8c-NaCl (0.500 g, 0.557 mmol) in dmsO (10 mL). The resultant solution was then stirred at room temperature for 15 h and the solvent evaporated to dryness under vacuum. The residue was washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and dried under vacuum to give 11 as an off-white solid (0.224 g, 45%). Anal. Calcd (%) for C<sub>30</sub>H<sub>44</sub>Cl<sub>2</sub>N<sub>4</sub>Na<sub>2</sub>O<sub>9</sub>PdS<sub>2</sub> (11·3H<sub>2</sub>O): C, 40.39; H, 4.97; N, 6.28; S, 7.19. Found: C, 40.47; H, 5.27; N, 6.43; S, 6.98. <sup>1</sup>H NMR (300 MHz, dmsO-d<sub>6</sub>):  $\delta$  7.56 (s, 2H, Imz-H<sup>4</sup>), 7.27 (s, 2H, Imz-H<sup>5</sup>), 7.13 (s, 2H, Ar-H<sup>3,5</sup>), 7.04 (s, 2H, Ar-H<sup>3,5</sup>), 3.90 (broad, 2H, NCH<sub>2</sub>), 2.92 (broad, 2H, NCH<sub>2</sub>), 2.37 (s, 6H, Ar-*p*-CH<sub>3</sub>), 2.20 (broad, 4H, CH<sub>2</sub>SO<sub>3</sub>), 2.13 (broad, 8H, Ar-*o*-CH<sub>3</sub> and CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> overlapping), 1.88 (broad, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.37 (s, 6H, Ar-*o*-CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, dmsO-d<sub>6</sub>):  $\delta$  158.6 (Imz-C<sup>2</sup>), 138.4 (Ar-C<sup>4</sup>), 136.8 (Ar-C<sup>2,6</sup>), 134.6 (Ar-C<sup>1</sup>), 133.6 (Ar-C<sup>2,6</sup>), 128.8 and 128.6 (Ar-C<sup>3,5</sup>), 123.6 (Imz-C<sup>5</sup>), 120.9 (Imz-C<sup>4</sup>), 48.2 (NCH<sub>2</sub>), 47.9 (CH<sub>2</sub>SO<sub>3</sub>), 24.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 20.2 (Ar-*p*-CH<sub>3</sub>), 18.4 and 16.6 (Ar-*o*-CH<sub>3</sub>). ESI-MS (negative ion, MeOH) *m/z* (11: C<sub>30</sub>H<sub>38</sub>Cl<sub>2</sub>N<sub>4</sub>Na<sub>2</sub>O<sub>6</sub>PdS<sub>2</sub>): 755.0959 [11 - Cl-2Na]<sup>-</sup> (calcd 755.0962) 100%.

**Characterization Data for 11e.** A 0.16 M solution of HCl in diethyl ether (13.2 mL, 2.11 mmol) was added dropwise to a solution



of **8e**·NaCl (0.500 g, 0.527 mmol) in dmsO (10 mL). The resultant solution was stirred at room temperature for 1 h. This complex was not isolated. <sup>1</sup>H NMR (300 MHz, dmsO-*d*<sub>6</sub>): δ 7.36 (s, 1H, Imz-H<sup>4,5</sup>), 4.37 (broad, 1H, NCH<sub>2</sub>), 4.09 (broad, 1H, NCH<sub>2</sub>), 2.06, 1.95 (broad, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), CH<sub>2</sub>S under the solvent resonance. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, dmsO-*d*<sub>6</sub>): δ 157.8 (Imz-C<sup>2</sup>), 123.6 (Imz-C<sup>4,5</sup>), 50.7 (NCH<sub>2</sub>), 50.0 (CH<sub>2</sub>SO<sub>3</sub>), 27.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).

**Characterization Data for 12.** This complex was identified by comparison of its <sup>1</sup>H NMR spectrum with that reported previously.<sup>26</sup> Anal. Calcd (%) for C<sub>13</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>4</sub>Na<sub>2</sub>O<sub>9</sub>PdS<sub>2</sub> (12·3H<sub>2</sub>O): C, 23.38; H, 3.62; N, 8.39; S, 9.60. Found: C, 23.12; H, 3.83; N, 8.35; S, 9.86.

**General Procedure for the Suzuki–Miyaura Cross-Coupling Reactions.** All operations were performed under an argon atmosphere using deoxygenated water. Phenylboronic acid (0.077 g, 0.60 mmol) and the corresponding chloroarene (0.50 mmol; 0.25 mmol for **13e**) were stirred in an aqueous 0.75 M solution of sodium hydroxide (2 mL, 1.5 mmol) for 2 min at room temperature. After addition of catalyst **1a** (2.1 mg, 2.5 μmol, 0.5 mol %), the reaction mixture was vigorously stirred at 60 °C for the time specified in **Scheme 8** (see the **Supporting Information** for details). After cooling to room temperature, the reaction mixture was treated with an aqueous 3 M solution of HCl (1 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over MgSO<sub>4</sub> and the solvent evaporated to dryness under vacuum. The solids thus obtained were suspended in water (3 mL), ultrasonicated for 1 min, and centrifuged for 3 min at 3000 rpm to remove the excess of phenylboronic acid. The aqueous phase was decanted, the washing process repeated twice, and the white solids dried under vacuum. Isolated yields are given in **Scheme 8** (see the **Supporting Information** for details).

**X-ray Crystallographic Studies.** Suitable single crystals of **1a** were obtained by cooling a concentrated solution of the complex in a mixture of dmsO/acetone (1:10) overnight at 5 °C. A summary of crystal data, data collection, and refinement parameters for the structural analysis is given in **Table S2**. Crystals were glued to a glass fiber using an inert polyfluorinated oil and mounted in the low-temperature N<sub>2</sub> stream (200 K) of a Bruker-Nonius Kappa-CCD diffractometer equipped with an area detector and an Oxford Cryostream 700 unit. Intensities were collected using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were measured with exposure times of 20 s per frame (5 sets; 302 frames; phi/omega scans; 2.0° scan-width). Raw data were corrected for Lorenz and polarization effects. The structure was solved by direct methods, completed by subsequent difference Fourier techniques and refined by full-matrix least-squares on F<sup>2</sup> (SHELXL-97).<sup>41</sup> Anisotropic thermal parameters were used in the last cycles of refinement for the non-hydrogen atoms. Absorption correction procedures were carried out using the multiscan SORTAV (semiempirical from equivalent) program. Some disorder was detected and refined in the structure in one of the –SO<sub>3</sub> groups, in the central carbon atom of the allyl group, and in two of the coordinated dmsO molecules. Hydrogen atoms were included in the last cycle of refinement from geometrical calculations and refined using a riding model. All the calculations were made using the WINGX system.<sup>42</sup>

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00635.

<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, crystallographic data for **1a**, reactions with Brønsted acids, synthesis and spectroscopic characterization of **13a–e** (PDF)

### Accession Codes

CCDC 1570388 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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