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## Synthesis, characterization, photophysical properties, and catalytic activity of an SCS bis(N-heterocyclic thione) (SCS-NHT) Pd pincer complex†

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Treatment of 1,3-bis(3'-butylimidazolyl-1'-yl)benzene diiodide with elemental sulfur in the presence of a base produced a bis(N-heterocyclic thione) (NHT) pincer ligand precursor. Its reaction with  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  produced chloro[1,3-bis(3'-butylimidazole-2'-thione- $\kappa$ -S)benzene- $\kappa$ -C]palladium(II), a 6,6-fused ring SCS-NHT palladium pincer complex. This air stable compound is, to our knowledge, the first SCS pincer complex that utilizes N-heterocyclic thione (NHT) donor groups. The molecular structures of the ligand precursor and the palladium complex were determined by X-ray crystallography and computational studies provided insight into the interconversion between its *rac* and *meso* conformations. The photophysical properties of the complex were established, and its catalytic activity in Suzuki, Heck, and Sonogashira cross-coupling reactions was evaluated.

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## Introduction

Pincer complexes are a specific class of organometallic compounds containing a tridentate ligand in which a central moiety and two lateral donor groups bind to a metal center in a meridional fashion. Since their appearance in 1976,<sup>1</sup> pincer complexes have been extensively investigated due to their

inherent stability and due to the ease with which their electronic structure and reactivity may be tuned by varying the metal center or the flanking donor groups. This structural diversity has been exploited to generate a variety of pincer ligands and complexes, typically designated by the identity of the ligating atoms as PCP,<sup>1,2</sup> NCN,<sup>3–5</sup> POCOP,<sup>6,7</sup> PNP,<sup>8,9</sup> CNC,<sup>10,11</sup> CCC,<sup>12</sup> and so on.

The first SCS pincer complex, a thioether-based palladium(II) derivative, was reported by Shaw in 1980.<sup>13</sup> Sulfur-containing pincer ligands have been shown to exhibit a great deal of architectural diversity and variations in their design including lateral donors such as thioethers,<sup>14–21</sup> thioamides<sup>22–28</sup> or phosphine sulfides.<sup>29–31</sup> Although the chemistry of SCS pincer complexes is not as developed as that of the related PCP and NCN derivatives, they have been found to exhibit interesting photophysical properties<sup>22–24,26,30,32</sup> and catalytic applications ranging from the borylation of allylic alcohols<sup>33</sup> to a variety of cross-coupling reactions.<sup>17–19,34,35</sup> Additionally, thione and bis-thione ligands have been successfully applied in catalysis.<sup>36,37</sup>

It is noteworthy that pincer complexes incorporating N-heterocyclic thione (NHT) donor groups are virtually unknown even though the coordination chemistry of simple monodentate NHTs has been extensively investigated.<sup>38–40</sup> In this regard, the only metal complexes containing pincer-type ligands containing NHTs are the copper(I), copper(II), and zinc (II) compounds reported by Miecznikowski and coworkers<sup>41–45</sup>

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† Electronic supplementary information (ESI) available: Catalytic trials, CIF files, photophysical data, NMR spectra, ESI-TOF MS data, further computational details, an overlay image of experimental vs. computational molecular structure, and tables giving crystallographic data for compound 2 and complex 3. CCDC 978195 and 978196. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/C4DT03324H

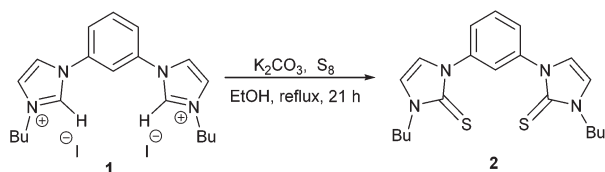
and the rhodium(i) and iridium(i) derivatives synthesized by Jia, Huang and Jin.<sup>46</sup>

Herein, we report the synthesis of a 1,3 phenylene-bridged bis(NHT) ligand precursor and its successful metalation, producing the first SCS pincer complex incorporating NHT groups. The photophysical properties (absorption, emission, photostability, and excited-state lifetime) of the complex, both in solution and in the solid state, are reported, along with its catalytic activity for Suzuki,<sup>47</sup> Heck,<sup>48</sup> and Sonogashira<sup>49</sup> cross-coupling reactions.

## Results and discussion

### 1,3-Bis(3'-butylimidazole-2'-thione)benzene

The synthesis of ligand precursor 1,3-bis(3'-butylimidazole-2'-thione)benzene (**2**), shown in Scheme 1, was achieved by refluxing a suspension of 1,3-bis(3'-butylimidazol-1'-yl)benzene diiodide (**1**),<sup>50</sup> K<sub>2</sub>CO<sub>3</sub>, and S<sub>8</sub> in ethanol under an argon atmosphere. Work-up yielded analytically pure product in 91% yield. The most salient feature in the <sup>1</sup>H NMR spectrum of **2** is the disappearance of the singlet at 9.94 ppm observed for the methine proton flanked by two nitrogen atoms (*i.e.* NCHN) in the bis(imidazolium) precursor **1**. These data are consistent with the conversion of the bis(imidazolium) precursor to the bis(thione) **2**. The ligand precursor was also characterized by elemental analysis, <sup>13</sup>C NMR and FT-IR spectroscopies, and X-ray crystallography (*vide infra*). Experimental details and spectral data are available in the ESI.†

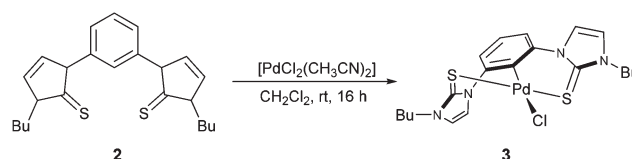


**Scheme 1** Synthesis of 1,3-bis(3'-butylimidazolyl-2'-thione)benzene (m-Bmb<sup>nBu</sup>, **2**).

### *Rac*-chloro[1,3-bis(3'-butylimidazole-2'-thione-κ-S)benzene-κ-C]palladium(II) · 1/2CH<sub>2</sub>Cl<sub>2</sub>

A variety of palladium sources were evaluated in preliminary experiments, which were monitored *via* <sup>1</sup>H NMR spectroscopy. When equimolar amounts of **2** and PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> were combined in CH<sub>2</sub>Cl<sub>2</sub> at room temperature (Scheme 2), X-ray quality crystals precipitated over the course of 16 h (see below). For bulk isolation, further optimization of the work-up procedure afforded analytically pure product in 67% yield. The disappearance of the triplet at 7.97 ppm in the <sup>1</sup>H NMR spectrum of **2** (assigned to the proton in the 2-position on the benzene ring) was consistent with metalation of the aryl ring. It also produced a downfield shift from 4.07 to 4.18 ppm of the triplet corresponding to the methylene protons α to the nitrogens. Additionally, in the <sup>13</sup>C NMR data there was an upfield shift of

the peak corresponding to the thiocarbonyl from 161.5 ppm in **2** to 154.9 ppm. Furthermore, the ESI-TOF MS exhibited a major peak at 491.0511 *m/z* corresponding to a [M – Cl]<sup>+</sup> fragment. In DMSO-*d*<sub>6</sub>, spectral line broadening was consistent with hemilabile NHTs. However, <sup>1</sup>H NMR spectra of **3** in CD<sub>2</sub>Cl<sub>2</sub> gave no indication of hemilability upon titration with up to 25 equiv. of DMSO as the only change observed was a small shift in the aromatic proton signal *para* to Pd, which was consistent with solvent perturbation (ESI). The Raman spectrum of **3** was collected using the 647 nm output of a Kr ion laser and methods described previously.<sup>51</sup> This spectrum agrees very well with theoretical predictions (see Fig. S18†).

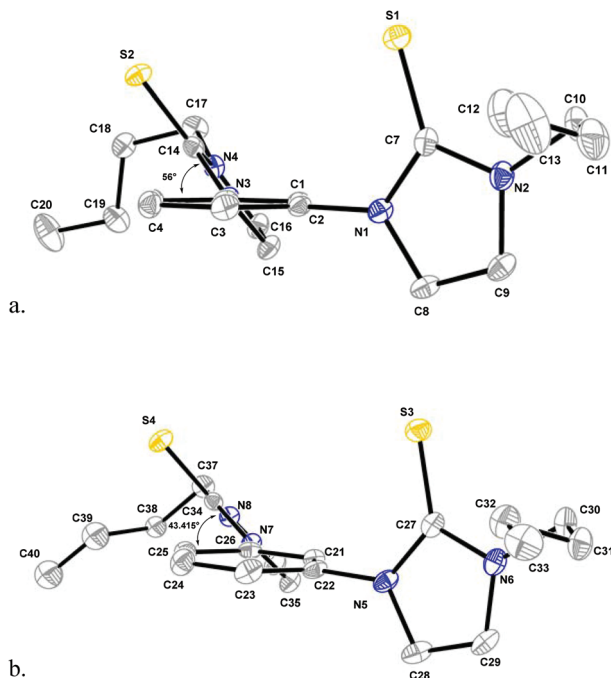


**Scheme 2** Preparation of *rac*-chloro[1,3-bis(3'-butylimidazole-2'-thione-κ-S)benzene-κ-C]palladium(II) · 1/2CH<sub>2</sub>Cl<sub>2</sub> (**3**).

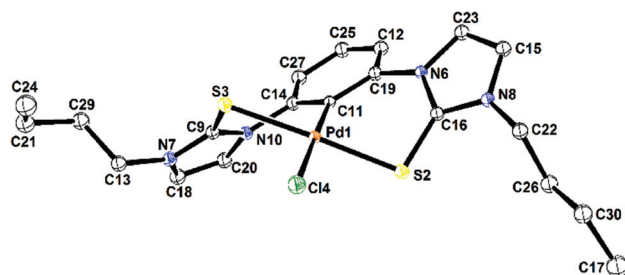
### Crystallography

The molecular structure of **2** determined by X-ray crystallography contained two molecules in the asymmetric unit. Although both molecules are in the *meso*-conformation, a difference of 12.6° in one of the C–S dihedral angles relative to the benzene rings was noted. The differences in dihedral angles may be observed in the edge-on views of the two molecules in the asymmetric unit (Fig. 1). Molecule **1a** (Fig. 1) contains dihedral angles of 55.7° and 86.6° while **1b** has dihedral angles of 43.4° and 92.9°. The disorder in the butyl group of molecule **1b** is also illustrated and displays the isotropic nature of the chain.

The molecular structure of complex **3** and its packing in the unit cell are shown in Fig. 2 and 3, respectively. The structure shown in Fig. 2 contains two 6,6-fused palladacycles in a twisted *rac*-conformation. The conformation of **3** contrasts with a previously reported SNS complex, which exhibited the *meso*-conformation due to the preferred tetrahedral geometry of the d<sup>10</sup> Zn metal center.<sup>43</sup> While it is similar to the *rac*-conformation of the S–N–S ligand reported in 5-coordinate Cu complexes.<sup>45</sup> This twisted *rac*-geometry (atropisomerism) is also in contrast with CCC–NHC complexes, which exhibit planar conformations of the 5,5-fused metallacycles.<sup>52–54</sup> Furthermore, the *rac*-conformation of **3** has a chiral twist similar to the 5,6-fused-ring systems reported by Odinet<sup>29</sup> and to the 5,5-fused-ring complexes synthesized by Kruithof and co-workers.<sup>55</sup> This conformational issue in pincer complexes was elegantly exploited by Protasiewicz to make twisted complexes.<sup>56</sup> Unlike the previously reported CNC–NHC–Pd and C<sup>∧</sup>C–NHC–Pd complexes reported by Crabtree,<sup>12</sup> which had measureable interconversion barriers for the atropisomers, no experimental evidence for other isomers was observed for **3** (see DFT computations). The square planar Pd geometry is maintained in **3**, with bond angles of 177.9° for S3–Pd1–S4



**Fig. 1** ORTEP diagrams the two molecules of **2** in the asymmetric unit with hydrogens omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å): S2–C14, 1.6758(18); S1–C7, 1.6842(18); S4–C34, 1.6837(18); S3–C27, 1.6858(18). Selected bond angles (°): C3–C2–N1–C7 = 86.6, C5–C6–N3–C14 = 55.7; C25–C26–N7–C34 = 43.4; C23–C24–N5–C27 = 92.9.

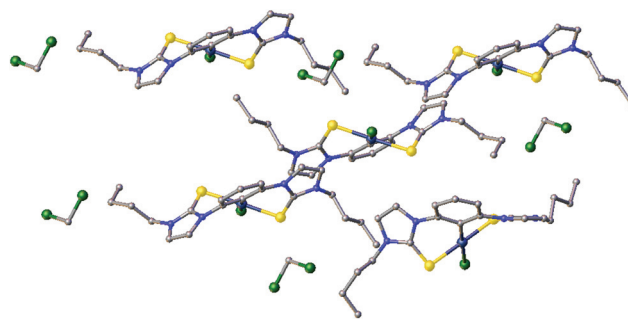


**Fig. 2** ORTEP diagram of **3** with hydrogens omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å): Pd1–S2, 2.2899(13); Pd1–S3, 2.3421(13); Pd1–Cl4, 2.4074(14); Pd1–C11, 1.991(5); S2–C16, 1.701(5); S3–C9, 1.703(5). Selected bond angles (°): C9–S3–Pd1, 96.7; S3–Pd1–S4, 177.9; S3–Pd1–C14, 89.9; S4–Pd1–C14, 88.5; C11–Pd1–Cl4, 178.8; C14–C11–Pd1–S3, –39.7; C19–C11–Pd1–S2, –42.1.

and 178.8° for C11–Pd1–Cl4. The Pd–S distances and other geometric data in the square plane are similar to other Pd NHT complexes.<sup>57–59</sup> The Pd–S distance is also in the same range as Pd–S distances in some thiolate complexes.<sup>60</sup>

### Photophysics

Photophysical properties of **3** were evaluated in solution and in the solid state. The solution data included absorption, emission, and lifetime measurements. UV/Vis absorption exhibited

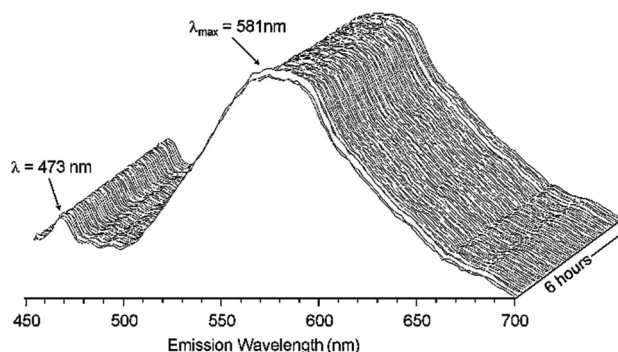


**Fig. 3** Crystal packing of complex **3** using Olex2.

a broad peak at 291 nm. Upon excitation at 355 nm, the emission spectrum contained a sharp peak at 473 nm. Complex **3** was found to have a lifetime that exhibited biexponential decay, suggesting competing electronic transitions. The lifetimes of **3** included  $\tau_1$  of  $0.60 \pm 0.06$  ns and  $\tau_2$  of  $3.91 \pm 0.31$  ns in MeOH and  $\tau_1$  of  $0.61 \pm 0.03$  ns and  $\tau_2$  of  $3.72 \pm 0.15$  ns in CHCl<sub>3</sub>. Photophysical data of **3** in the solid state included diffuse reflectance, emission lifetime, and photostability. The diffuse reflectance spectrum exhibited a sharp absorption at 350 nm. The emission lifetime was found to have  $\tau_1$  of  $0.58 \pm 0.05$  ns and  $\tau_2$  of  $20.74 \pm 6.21$  ns. For applications in OLEDs the long term stability of the emitter has a direct impact on the lifetime of the electronic device in which it performs. The photostability of SCS–Pt complex **3** (Fig. 4) was measured using a 355 nm excitation source, and it exhibited 96% retention over 6 hours of constant excitation with emission peaks at 581 nm and 473 nm in ambient air. The retention of intensity in the emission spectrum indicates that the complex is not decomposed by ambient oxygen or water even with UV excitation. This level of retention is comparable to the best reports.<sup>52</sup>

### DFT computations

The ligand conformations observed in the crystal structures of **2**, **3**, and the aforementioned SNS Zn complex<sup>43</sup> were significantly varied. Compound **2** and the SNS Zn complex were



**Fig. 4** Photostability of **3** in the solid state.

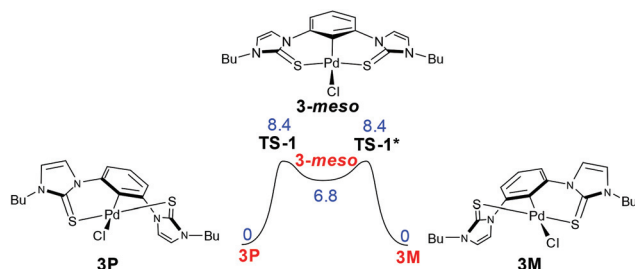


Fig. 5 Computed B3LYP energies ( $\text{kcal mol}^{-1}$ ) of *rac*- and *meso*-conformations: **3P**, **3M**, and **3-meso**.

observed to have a *meso*-conformation (Fig. 1). However, complex **3** was found to have the *rac*-conformation (Fig. 2). While in DMSO standard solvent-assisted displacement of the NHTs would pertain (see NMR discussion above), in  $\text{CH}_2\text{Cl}_2$  this pathway is much less likely. Because there was no experimental evidence of other isomers of **3**, DFT computations were used to gain insight into the issue of enantiomer *versus* diastereomer stability and interconversion, which yielded a proposed intramolecular isomerization pathway that is lowest in energy (Fig. 5). The results of the DFT geometry optimizations for **3P**, **3M**, and **3-meso** are illustrated in Fig. 5. The B3LYP-optimized geometry of **3** compared favourably with the molecular geometry from the X-ray structure determination. The  $\Delta G_{\text{comp}}^\circ$  of **3-meso** was computed to be  $6.8 \text{ kcal mol}^{-1}$  higher than **3-rac**. The  $\Delta G_{\text{comp}}^\ddagger$  from **3-rac** through **TS-1** to **3-meso** was determined to be  $8.4 \text{ kcal mol}^{-1}$ . These results indicate a high preference of the **3-rac** over the **3-meso** conformation and are consistent with the experimental observations.<sup>61</sup> This preference is attributable to the angle strain engendered by *cis*-ring fusion in the *meso*-conformation at the square planar metal (*rac*:  $90.2^\circ$  vs. *meso*:  $97.9^\circ$ ). Additional computational results for the PBEPBE functional are available in the ESI.†

### Catalytic activity

Palladium catalyzed cross coupling reactions are powerful tools in the synthetic chemist's arsenal.<sup>62</sup> Several recent examples include catalysts with sulphur-based ligands,<sup>63,64</sup> including NHT's.<sup>57</sup> Therefore, the catalytic activity of **3** was evaluated in several cross coupling reactions. Heck,<sup>34</sup> Suzuki–Miyaura,<sup>65</sup> and Sonogashira<sup>66</sup> reactions were investigated by treatment of iodobenzene with substrates for each and the results are displayed in Table 1. In the Heck reactions of iodobenzene and butyl acrylate or methyl methacrylate, modest yields were obtained in 52 h (Table 1, entries 1 and 2). The Suzuki–Miyaura reactions of phenyl boronic acid or *p*-tolyl boronic acid yielded the desired coupling products in yields of 74% and 67% in 48 h (Table 1, entries 3 and 4). In the Sonogashira reaction, diphenylacetylene was obtained in 58% yield in 18 h (Table 1, entry 5). When begun these reactions were yellow, and became cloudy yellow to dark red during the course of time. Explicitly, the catalytic trials did not become black. ESI-MS data were collected on samples taken during a

Table 1 Heck, Suzuki–Miyaura, and Sonogashira coupling reactions catalysed by **3** with 2 mol% loading

Entry	Products	Time	Yield <sup>a</sup> (%)
1 <sup>b</sup>		52 h	42
2 <sup>b</sup>		52 h	63
3 <sup>c</sup>		48 h	74
4 <sup>c</sup>		48 h	67
5 <sup>d</sup>		18 h	58

<sup>a</sup> Yields were obtained by GC/MS and toluene was used as an internal standard. All reactions were carried out in air at  $80^\circ\text{C}$  using 2 mol% of **3**. <sup>b</sup> Iodobenzene (1.0 mmol), substrate (2.0 mmol),  $\text{Et}_3\text{N}$  (1.0 mmol), DMF (0.7 M). <sup>c</sup> Iodobenzene (1.0 mmol), substrate (1.5 mmol),  $\text{Cs}_2\text{CO}_3$  (2.0 mmol), dioxane (0.12 M). <sup>d</sup> Iodobenzene (1.0 mmol), phenylacetylene (1.2 mmol),  $\text{CuI}$  (2 mol%),  $\text{Cs}_2\text{CO}_3$  (2.0 mmol), and DMSO (0.12 M).

catalytic run, and consistent with the physical observations, no evidence was found for the formation of nanoparticles or Pd clusters (see ESI and Fig. S21†). Much work has gone into determining the mechanisms of these reactions, and the very best catalysts produce stable Pd nanoparticles.<sup>67–73</sup> It is possible that compound **3** acts as a pre-catalyst as has been found for many palladium complexes.<sup>67,74</sup> Since the activity of **3** was found to be modest, no further examinations were made regarding the nature of the catalytically active species.<sup>75</sup>

## Conclusions

The first entries into a new class of tridentate ligands, an SCS-NHT pincer ligand precursor and its Pd complex, have been synthesized and fully characterized. The molecular structure of **3**, determined by X-ray crystallography, exhibited a *rac*-conformation that produced a chiral twist in the molecule while maintaining the square planar geometry of the metal center. The photophysics of the complex were evaluated in solution and in the solid state, with the complex demonstrating excellent solid state photostability in ambient air with 96% retention of emission intensity over 7 hours of constant excitation. B3LYP DFT computations were used to provide insight into the interconversion between *rac*- and *meso*-conformations and the stereochemical stability. The computations indicated a high preference for the *rac*- over the *meso*-conformation by  $6.8 \text{ kcal mol}^{-1}$ , which was consistent with experimental observations. Complex **3** was shown to be a versatile catalyst in Heck, Suzuki–Miyaura, and Sonogashira coupling reactions providing modest to good yields. Work to expand the SCS-NHT pincer family to include metals of biological significance is underway.



## Experimental section

### 1,3-Bis(3'-butylimidazolyl-2'-thione)benzene (2)

Under an argon atmosphere, a stirred suspension of **1** (7.06 g, 12.2 mmol), K<sub>2</sub>CO<sub>3</sub> (4.02 g, 29.1 mmol), S<sub>8</sub> (0.906 g, 28.3 mmol), and ethanol (200 mL) were refluxed for 21 h. The reaction mixture was removed from heat and the solvent was removed under reduced pressure to give a yellow solid. The solid was extracted with CH<sub>2</sub>Cl<sub>2</sub> (220 mL) and the filtrate was concentrated under reduced pressure to ~5 mL and pentane (30 mL) was added to give an off-white solid, which was collected by filtration and dried *in vacuo* for 24 h (4.31 g, 91%). Mp = 132–133 °C. Single crystals were grown *via* slow evaporation of a saturated solution of **2** in THF. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 8.00 (t, <sup>4</sup>J<sub>H-H</sub> = 2.0 Hz, 1H, C<sub>6</sub>H<sub>4</sub>), 7.59–7.79 (AB<sub>2</sub> pattern, 3H, C<sub>6</sub>H<sub>4</sub>), 7.46 (d, <sup>3</sup>J<sub>H-H</sub> = 2.6 Hz, 2H, imidazole H), 7.40 (d, <sup>3</sup>J<sub>H-H</sub> = 2.6 Hz, 2H, imidazole H), 4.03 (t, <sup>3</sup>J<sub>H-H</sub> = 7.3 Hz, 4H, CH<sub>2</sub>), 1.72 (quintet, <sup>3</sup>J<sub>H-H</sub> = 7.4 Hz, 4H, CH<sub>2</sub>), 1.33 (sextet, <sup>3</sup>J<sub>H-H</sub> = 7.4 Hz, 4H, CH<sub>2</sub>), 0.93 (t, <sup>3</sup>J<sub>H-H</sub> = 7.3 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (75.5 MHz, DMSO-*d*<sub>6</sub>): δ 161.5 (s, 2 C, C=S), 138.2 (d, <sup>2</sup>J<sub>C-H</sub> = 9, 2 C, C<sub>6</sub>H<sub>4</sub>), 128.9 (d, <sup>1</sup>J<sub>C-H</sub> = 165, 1 C, C<sub>6</sub>H<sub>4</sub>), 124.7 (dt, <sup>1</sup>J<sub>C-H</sub> = 6, 2 C, C<sub>6</sub>H<sub>4</sub>), 122.6 (d, <sup>1</sup>J<sub>C-H</sub> = 166, 1 C, C<sub>6</sub>H<sub>4</sub>), 118.8 (dd, <sup>1</sup>J<sub>C-H</sub> = 199, <sup>2</sup>J<sub>C-H</sub> = 10, 2 C, imidazole C), 118.0 (dd, <sup>1</sup>J<sub>C-H</sub> = 201, <sup>2</sup>J<sub>C-H</sub> = 10, 2 C, imidazole C), 46.7 (t, <sup>1</sup>J<sub>C-H</sub> = 141, 2 C, CH<sub>2</sub>), 30.2 (t, <sup>1</sup>J<sub>C-H</sub> = 127, 2 C, CH<sub>2</sub>), 19.2 (t, <sup>1</sup>J<sub>C-H</sub> = 125, 2 C, CH<sub>2</sub>), 13.6 (q, <sup>1</sup>J<sub>C-H</sub> = 125, 2 C, CH<sub>3</sub>). IR data: 3118 (w), 3086 (m), 2958 (m), 2937 (m), 2873 (w), 1602 (m), 1565 (w), 1494 (m), 1459 (m), 1415 (s), 1398 (vs), 1354 (m), 1313 (m), 1297 (w), 1287 (w), 1261 (s), 1233 (s), 1194 (m), 1151 (s), 1115 (w), 1096 (w), 1079 (w), 1032 (w), 980 (w), 940 (w), 902 (w), 883 (m), 821 (w), 799 (m), 774 (s), 743 (m), 717 (s), 687 (vs), 673 (vs). Anal. Calc. for C<sub>20</sub>H<sub>26</sub>N<sub>4</sub>S<sub>2</sub>: C, 62.14; H, 6.78; N, 14.49%. Found: C, 62.16; H, 6.73; N, 14.48%.

### Rac-chloro[1,3-bis(3'-butylimidazole-2'-thione-κ-S)benzene-κ-C]-palladium(II)-1/2CH<sub>2</sub>Cl<sub>2</sub> (3)

In a round bottom flask, **2** (2.13 g, 5.51 mmol), [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (1.34 g, 5.51 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (260 mL) were combined and stirred at room temperature for 16 h. The reaction mixture was filtered to afford a dark red solution. The solution was concentrated under reduced pressure to afford a dark red, crystalline solid. The red solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and the solution was washed with distilled water (3 × 350 mL). The organic layer was concentrated to ~150 mL to precipitate a yellow-orange solid. The yellow-orange solid was collected by filtration and washed with acetone to produce a yellow powder, which was dried under vacuum (1.82 g, 67%). Single crystals were grown *via* vapor diffusion of Et<sub>2</sub>O into a saturated solution of **3** in CH<sub>2</sub>Cl<sub>2</sub>. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.29 (d, *J* = 2.3 Hz, 2H), 7.26 (t, *J* = 8.2 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 2.4 Hz, 2H), 5.33 (s, 1H), 4.18 (t, *J* = 7.4 Hz, 4H), 1.84 (m, *J* = 2.0 Hz, 4H), 1.44 (m, *J* = 7.6 Hz, 4H), 0.98 (t, *J* = 7.4 Hz, 6H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 154.9, 140.0, 133.7, 126.4, 121.7, 119.8, 118.4, 49.7, 31.9, 20.3, 14.0. Anal. Calc. for C<sub>20</sub>H<sub>25</sub>ClN<sub>4</sub>PdS<sub>2</sub>·1/2CH<sub>2</sub>Cl<sub>2</sub>: C, 43.20; H, 4.60; N, 9.83. Found: C, 43.43; H, 4.66; N, 9.94%.

## DFT computational methods

Theoretical calculations have been carried out using the Gaussian09<sup>76</sup> implementations of PBEPBE (the PBE exchange and correlation functionals<sup>77,78</sup>) and B3LYP (the B3 exchange functional<sup>79</sup> and LYP correlation functional<sup>80</sup>) density functional theory (DFT),<sup>81</sup> using non-default unpruned fine grids for energies (75, 302), non-default unpruned coarse grids for gradients and Hessians (35, 110), and non-default SCF convergence for geometry optimizations (10<sup>-6</sup>). All geometry optimizations were conducted with the same basis set combination. The basis set for palladium (341,341,31) → [3s3p2d] was the Hay and Wadt basis set (BS) and effective core potential (ECP) combination (LanL2DZ)<sup>82</sup> as modified by Couty and Hall, where the two outermost p functions have been replaced by a (41) split of the optimized palladium 5p function.<sup>83</sup> The basis sets for chlorine and sulfur were the LanL2DZ(d,p)<sup>84,85</sup> BS/ECP combinations. The 6-31G(d') basis sets<sup>86–88</sup> were used for all nitrogens, carbons, and hydrogens. Spherical harmonic d functions were used throughout, *i.e.*, there are five angular basis functions per d function. For comparison with the X-ray crystal structure data, the full ligand was used. All structures were fully optimized, and analytical frequency calculations were performed on all structures (zero, one, or two imaginary frequencies confirm a local minimum (zeroth-order saddle point), a transition state (first-order saddle point), or second-order saddle point. All energies, enthalpies, and Gibbs free energies reported have been calculated using standard conditions (298.15 K and 1 atm). Both IR and Raman intensities were computed.

## Diffuse reflectance

Solid state absorbance (diffuse reflectance) was taken by directing the emission of a Xenon arc lamp on the sample using a solarization resistant fiber optic cable. The sample was placed inside an IC2 integrating sphere from Stellar Net Inc. and the fiber optic was connected to the illuminator input port. A second fiber optic cable was used to collect light from inside the integrating sphere and direct it to an OceanOptics spectrometer. The collected spectrum was compared to a standard composed of Spectralon® in order to determine the percent reflectivity of the sample.

## Absorption/emission

The solution phase UV-vis absorption spectrum was collected using a Hewlett Packard 8453 UV-Vis spectrometer with a 1 second integration time and 1 nm resolution over the range 200–800 nm. The solution phase emission spectrum was collected using a PerkinElmer LS 55 fluorescence spectrometer. The excitation wavelength was chosen to be 355 nm with a 100 nm min<sup>-1</sup> scan rate.

## Lifetime

The solution phase lifetime was determined to be less than 20 ns using the second harmonic (532 nm) of a pulsed Nd:YAG laser. Further lifetime measurements were made using 405 nm

excitation source from a pulsed diode laser. Lifetime data was taken in the solid state as well as in solution in methanol or in chloroform. Emission from the sample was collected using a fiber optic cable and spectra were collected using a PDM detector from PicoQuant.

### Photostability

Photostability was measured using a xenon arc lamp and monochromator to select 355 nm as the excitation source. Emission was collected using a fiber optic cable and detected using a photodiode array (PDA). Spectra were collected every 30 seconds for 7 hours and 17 minutes.

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