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Ligand Rearrangement Leads to Tetrahydrothiophene-Functionalized N,S-Heterocyclic Carbene Palladium(II) Complexes

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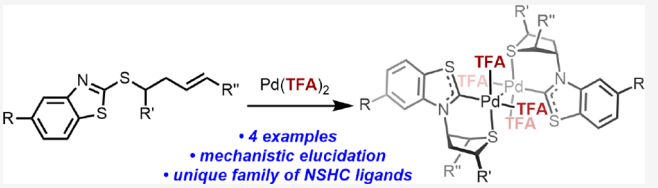
ABSTRACT: Tetrahydrothiophene-functionalized N,S-heterocyclic carbene palladium(II) complexes are synthesized through an unexpected rearrangement that proceeds with palladium(II) trifluoroacetate but not with palladium(II) acetate, palladium(II) bromide, or palladium(II) chloride. A series of these complexes were isolated and characterized by X-ray crystallography. The mechanism of formation of these [3.2.1]palladabicycles was explored, and the catalytic capabilities of these complexes were demonstrated in representative C−C coupling reactions.

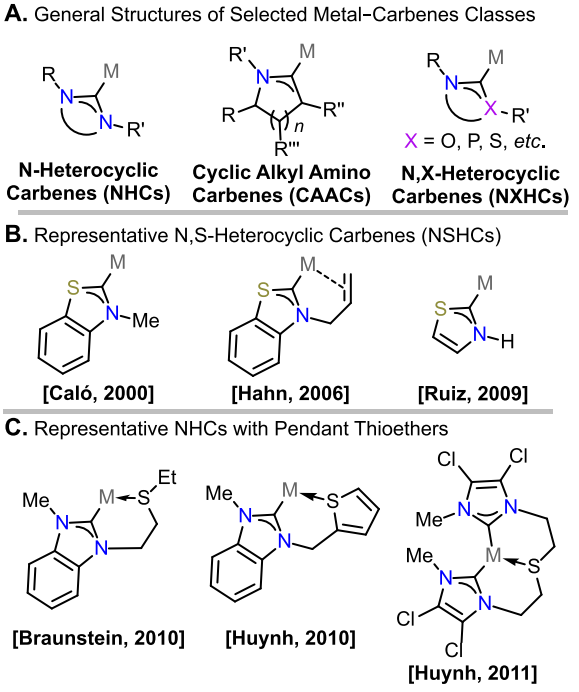


INTRODUCTION

The past few decades have witnessed a surge of interest in carbenes as spectator ligands in transition-metal catalysis.[1] An increasingly vast collection of ligands, including N-heterocyclic carbenes (NHCs),[2] cyclic (alkyl)- and (aryl)(amino)carbenes (CAACs),[3] and abnormal NHCs (*a*NHCs),[4] have been developed that collectively grant access to diverse steric and electronic properties useful in catalyst development (Scheme 1A). While much of the research on NHC−metal complexes has focused on those in which the metal is coordinated to the C atom between two nitrogen atoms in an imidazole-based framework,[1d,2i] interest in similar carbenes,[5] such as those where one N atom is replaced with an O (oxazole), P (phosphazole), or S atom (thiazole) has led to the naming system N,X-heterocyclic carbenes (X = O, P, S, etc.) or NXHC (Scheme 1B).[6] NXHC−metal complexes have been extensively explored,[7] with a number of studies being focused specifically on NSHC−metal complexes.[6]

Polydentate ligands containing either multiple tethered NHCs or an NHC and an additional pendant functional group, such as an aminophosphine,[8] an ester,[9] or others,[10] have also been synthetically explored. Notably, a number of palladium complexes bearing sulfur-containing NHCs have been characterized (Scheme 1C)[11] and shown to catalyze various reactions, such as Suzuki−Miyaura couplings,[12] Mizoroki−Heck reactions,[13] asymmetric allylic alkylations,[14] hydroaminations,[15] direct arylations,[15b,16] Sonogashira couplings,[17] and nitrile−amide interconversions.[17] In catalysis, metal-bound thioethers are hemilabile ligands that exhibit reversible binding to the metal center when they are incorporated in a polydentate ligand framework that contains one or multiple NHCs; this property can be useful in ligand design, for example in stabilizing resting states while still allowing dissociation to open a coordination site for the association of reactants.[11d,15b,18]

Scheme 1. Examples of Relevant Carbenes



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RESULTS AND DISCUSSION

During the course of a previous study,[19] a mixture of 2-(but-3-en-1-ylthio)benzo[*d*]thiazole (**1a**) and palladium(II) trifluoroacetate ($Pd(TFA)_2$) was stirred at 45 °C in 1,2-dichloroethane (1,2-DCE) for 12 h in an attempt to isolate a palladium species bound to both the benzothiazole directing group and the pendant alkene. After vapor diffusion of diethyl ether into the solution, a large number of yellow crystals formed. X-ray analysis revealed these crystals to be composed of an unexpected dimeric $Pd_2(NSHC)_2(TFA)_4$ complex containing the C,S-bidentate bridging NSHC ligand 3-(tetrahydrothiophen-3-yl)benzo[*d*]thiazol-3-ium-2-ide (Figure 1). This product, (±)-**2a**, was isolated in 82% yield, and its structure was further confirmed by ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectrometry (HRMS). As of yet, a palladium complex with this type of bidentate ligand based on an NSHC with a pendant thioether has not been reported, to the best of our knowledge. Notably, when other palladium sources were used, $PdBr_2$, $PdCl_2$, and $Pd(OAc)_2$, this product was not observed, suggesting that trifluoroacetate (TFA) ligands are uniquely suited for the formation of the NSHC complex (Table 1). This may be attributed to the highly electrophilic nature of the Pd center in $Pd(TFA)_2$, which may promote key steps in the rearrangement process (*vide infra*).

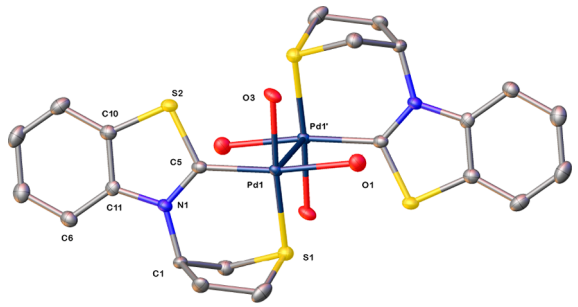
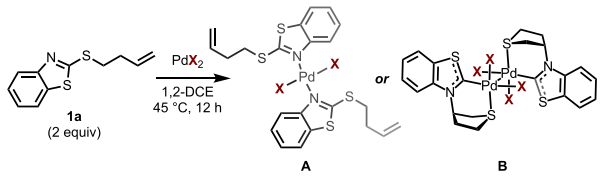


Figure 1. Molecular structure of (±)-**2a** showing 50% probability ellipsoids. Hydrogen atoms and $(CO)CF_3$ groups from trifluoroacetate ligands are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Pd1–Pd1′ 3.2086(5), Pd1–S1 2.2581(10), N1–C1 1.482(5), N1–C5 1.332(5), N1–C11 1.407(5), S2–C5 1.711(4), S2–C10 1.736(4), S1–Pd1–C5 94.21(11), C5–Pd1–O3 90.14(13), O3–Pd1–O1 83.25(11), O1–Pd1–S1 92.48(8), C5–Pd1–Pd1′ 91.49(10).

This complex was of interest from both a structural and a mechanistic perspective. First, the formation of a bridged [3.2.1]palladabicycle containing a five-membered tetrahydrothiophene ring is a unique structure combining both an NSHC and a pendant bridging cyclic thioether. Second, the significant rearrangement of the starting material, which involves the breaking of a C(benzothiazole)–S(thioether) bond and the formation of C–S and C–N bonds, requires an unusual mechanism. Furthermore, due to the previously demonstrated synthetic utility of this benzothiazole thioether directing group,[19] a greater understanding of this mechanism could lead to further applications in reaction development.

Finding this complex and its formation interesting, we sought to synthesize and characterize several similar compounds to understand the generality and limitations of this process (Scheme 2). (*S*)-2-(Pent-4-en-2-ylthio)benzo[*d*]thiazole ((*S*)-**1b**), which was added in a 2:1 ratio relative to $Pd(TFA)_2$, successfully provided product **2b** (70% yield) (Scheme 2A), isolated as a mixture of diastereomers (dr = 1.4:1, as determined by ^{1}H NMR of the bulk solid). The ^{1}H NMR spectrum of this mixture shows that only two major species are present in solution, suggesting that this series of palladium complexes, while being Pd–Pd dimers in the solid state, are monomeric in solution, since three diastereomeric species would be expected in the case of dimers. Furthermore, the Pd–Pd bond lengths of all the dimers in crystal form are

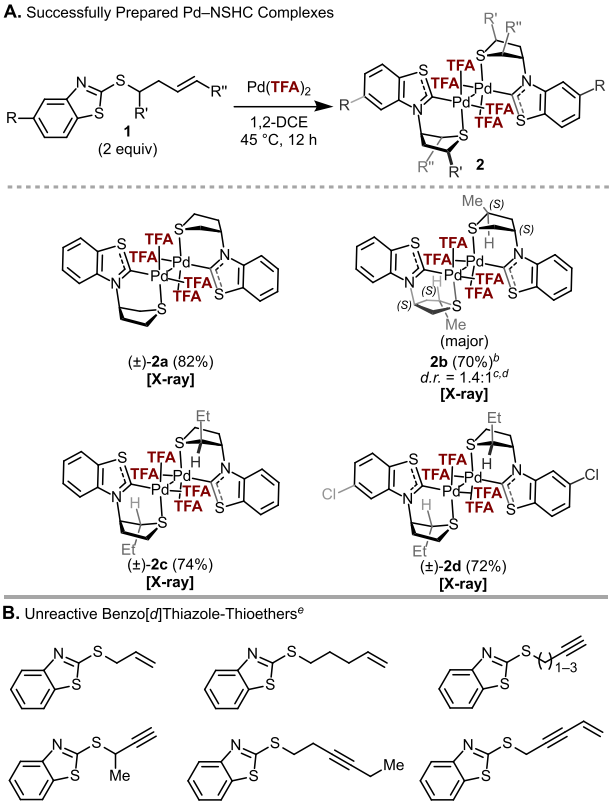
Table 1. Synthesis of Bidentate NSHC $Pd(TFA)_2$ Complexes[a]



PdX_2	A (%)	B (%)
$Pd(TFA)_2$	0[b]	**82**
$PdBr_2$	46	0[b]
$PdCl_2$	51	0[b]
$Pd(OAc)_2$	<5[c]	0[b]

[a]Isolated yields calculated as percentage of total possible product. [b]None isolated. [c]Observed only by ^{1}H NMR as part of a complex mixture of unassignable compounds.

Scheme 2. Scope and Limitations of Ligand Rearrangement[a]



[a]Isolated yields calculated as percentage of total possible dimer. [b]Product from (*S*)-2-(pent-4-en-2-ylthio)benzo[*d*]thiazole. [c]*d.r.* = Diastereomeric ratio. [d]A diastereomeric ratio of 3.3:1 was seen for the racemic product, due likely to solubility differences during crystallization. [e]Reaction conditions: $Pd(TFA)_2$ (1 equiv), benzo[*d*]-thiazole thioether (2 equiv), 1,2-DCE, 45 °C, 12 h, air.

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above 3.2 Å, suggesting semicoordination that would not persist in the presence of solvent (see Table S56 in the Supporting Information). From this sample of **2b**, selective crystallization of the major *S,S;S,S* diastereomer allowed for further characterization by X-ray crystallography.[20] These findings suggest that the stereochemistry at the carbon−sulfur bond of the thioether in the starting material is maintained during the rearrangement, with the diastereoselectivity established in the bond-forming step between C1 (the carbon γ to the sulfur of the thioether in the starting material) and N1 with the major diastereomer favored due to attenuated steric interactions between the methyl group and palladium (Figure 2).

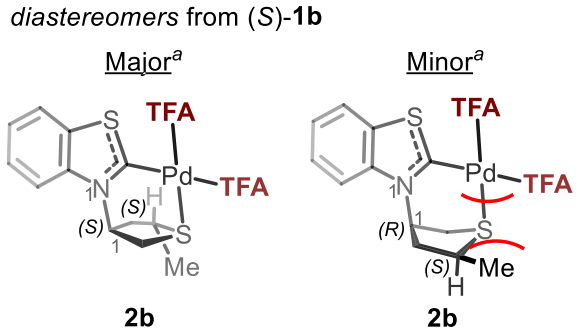
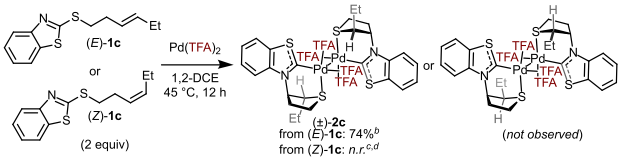


Figure 2. Two diastereomers formed in a 1.36:1 ratio, respectively, from the reaction of (*S*)-**1b** when the bulk solid was analyzed by ^{1}H NMR. Legend: (a) major and minor diastereomers observed, respectively, and identified by ^{1}H NMR and NOESY.

Next, (*E*)-2-(hex-3-en-1-ylthio)benzo[*d*]thiazole ((*E*)-**1c**), which was added in a 2:1 ratio relative to $Pd(TFA)_2$, successfully provided complex (±)-**2c** (74% yield) (Scheme 2A). Analysis of the bulk solid by ^{1}H NMR showed that this reaction yielded a single diastereomer, and X-ray analysis of a single crystal confirmed this to be the $Pd(TFA)_2$ complex with the bidentate *trans*-3-(2-ethyltetrahydrothiophen-3-yl)-benzo-[*d*]thiazole-3-ium-2-ide ligand. Notably, (*Z*)-2-(hex-3-en-1-ylthio)benzo[*d*]thiazole ((*Z*)-**1c**) does not provide any product for reasons that are not immediately obvious (Scheme 3). Additionally, (*E*)-5-chloro-2-(hex-3-en-1-ylthio)benzo[*d*]-

Scheme 3. Reactivity of *E* versus *Z* Internal Alkenes[a]



[a]Isolated yields calculated as percentage of total possible dimer. [b]Reaction conditions: $Pd(TFA)_2$ (1 equiv), (*E*)-2-(hex-3-en-1-ylthio)benzo[*d*]thiazole (2 equiv), 1,2-DCE, 45 °C, 12 h, air. [c]Reaction conditions: $Pd(TFA)_2$ (1 equiv), (*Z*)-2-(hex-3-en-1-ylthio)benzo[*d*]thiazole (2 equiv), 1,2-DCE, 45 °C, 12 h, air. [d]No reaction.

thiazole (**1d**) was also subjected to the same conditions, and complex (±)-**2d** was isolated (72% yield) (Scheme 2A). No analogous complexes were observed in attempts to use S-substituted benzo[*d*]thiazoles bearing internal or terminal alkynyl groups, longer or shorter tethers to the alkene, or 1,1-disubstituted terminal alkenes (Scheme 2B).

In order to gain insight into the rearrangement mechanism, we revisited the results in Table 1 to more rigorously characterize the coordination mode of the substrates in nonrearranged complexes containing other counterions. Notably, *trans*-$PdBr_2(\mathbf{1a})_2$ (complex **3a**) contains two molecules of the starting material coordinated through nitrogen (Figure 3). The analogous product **3b** was also

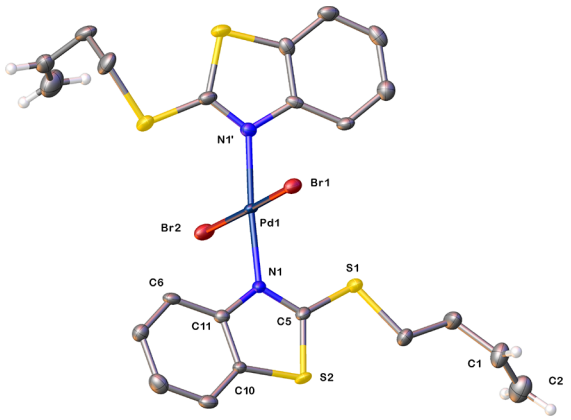
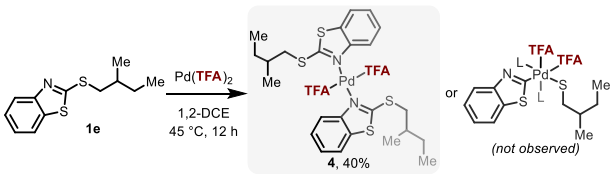


Figure 3. Molecular structure of **3a** showing 50% probability ellipsoids; hydrogen atoms not on alkene are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Pd1−N1 2.017(4), N1−C5 1.311(7), N1−C11 1.405(7), S2−C5 1.738(6), S2−C10 1.741(6), N1−Pd1−Br1 88.81(13), N1−Pd1−Br2 90.61(13), N1′−Pd1−Br1 88.90(13), N1′−Pd1−Br2 91.86(13).

observed with $PdCl_2$ (see Table 1 and Figure S11 in the Supporting Information). Under the same conditions, treating $Pd(TFA)_2$ with 2-((2-methylbutyl)thio)benzo[*d*]thiazole (**1e**), which contains no alkene, provides the corresponding structure, **4** (Scheme 4). Of note, no evidence of palladium

Scheme 4. $Pd(TFA)_2$ Coordination to Benzo[*d*]thiazole[a]



[a]Isolated yield.

C5(benzothiazole)−S1(thioether) insertion was observed, which suggests that C5(benzothiazole)−S1(thioether) oxidative addition occurs after cyclization onto the alkene. Next, we tested whether other transition metals can trigger this cyclization. To this end, **1a** was treated with numerous commercially available salts, including those derived from nickel, copper, platinum, iron, ruthenium, and silver. From these experiments, we obtained a novel silver complex from the treatment of **1a** (2 equiv) with silver(I) trifluoromethanesulfonate (AgOTf), which provided complex **5** (Figure 4). In the solid-state structure, Ag(I) is simultaneously bound to the thioether, the corresponding alkene, and the nitrogen of the benzothiazole group in a bimetallic dimer form, establishing that late transition metals can indeed coordinate to the alkene moiety in the presence of a benzothiazole group. Finally, consistent with a recent literature report,[21] we found that the treatment of **1a** with an iodine source leads the substrate to

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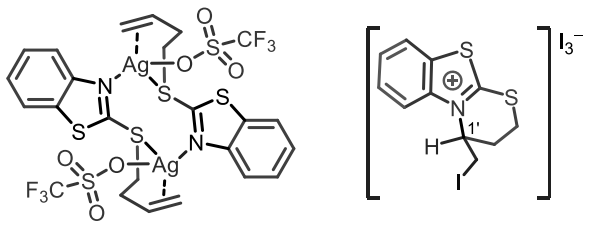


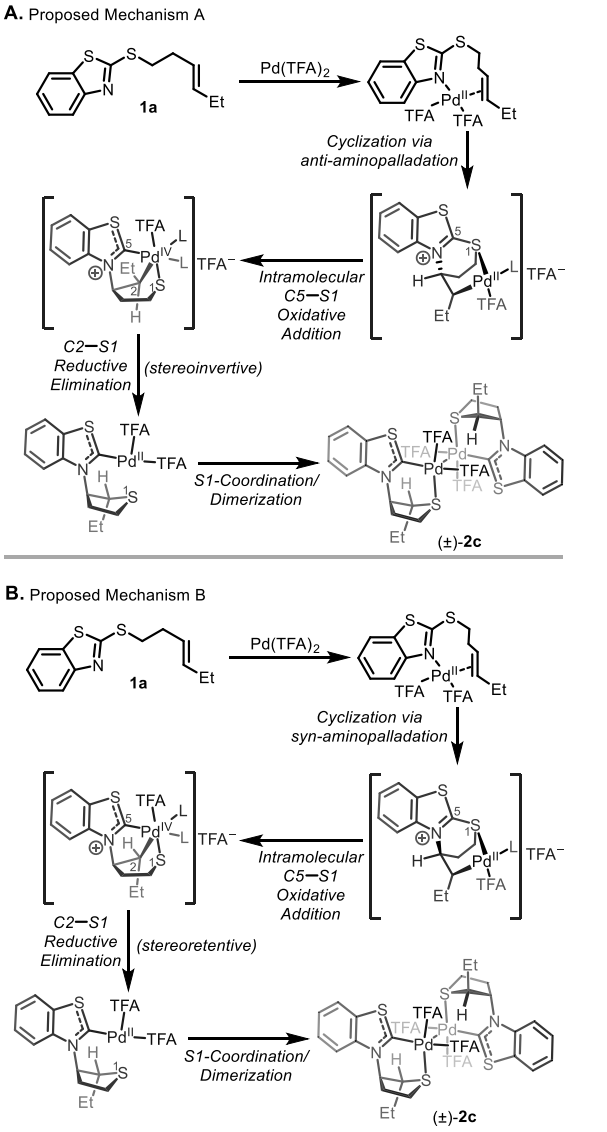
Figure 4. Isolated compounds with relevance to the proposed mechanisms.

undergo iodocyclization through nitrogen to give compound **6** (Figure 4).

On the basis of these initial results, several possible mechanisms of formation can be envisioned. Herein we describe two plausible pathways. In both proposals, we suggest that the $Pd(TFA)_2$ first coordinates to the starting material through the benzothiazole nitrogen and the alkene, as was previously computationally determined for the same starting material in an oxidative-Heck reaction with $Pd(OAc)_2$.[19] While in principle this coordination could alternatively proceed through the thioether, as is seen in complex **5**, or through a manner akin to that in complexes **3a**, **3b**, and **4**, in which the Pd coordinates only to the benzo[*d*]thiazole nitrogen and not the alkene, the time course data suggest that an N1-bound Pd(II) species coordinated to the alkene is the major species in solution (*vide infra*). After substrate coordination, the first mechanistic proposal involves a cyclization via *anti*-aminopalladation, with the benzothiazole nitrogen acting as the nucleophile, similar to the known cyclization induced by iodine. This cyclization step most likely requires a highly electrophilic Pd, which explains the unique reactivity observed with $Pd(TFA)_2$ over $Pd(OAc)_2$, $PdBr_2$, and $PdCl_2$. This could then be followed by intramolecular oxidative addition into the now weakened C5(benzothiazole)−S1(thioether) bond.[22] Following this, a C2(sp^3)−S1 S_N2-type reductive elimination would need to occur in a stereoinvertive fashion, as has been observed previously in C(sp^3)−heteroatom reductive elimination from Pd(IV) centers.[23] This inversion would provide the observed final product upon S1 coordination and complex dimerization (Scheme 5A). Alternatively, a cyclization could occur first through a *syn*-aminopalladation that, when it is followed by oxidative addition into the C5(benzothiazole)−S1(thioether) bond and stereoretentive C2(sp^3)−S1 reductive elimination, would lead to the observed product upon thioether coordination and dimerization (Scheme 5B).

To further probe the viability of the proposed mechanisms, we monitored the reaction progress over time with two model substrates, **1a** and **1c**, at 45 °C in air in $CDCl_3$ by setting up a series of parallel trials and halting them at predetermined time points; we then assayed the solution ($CDCl_3$) and precipitate (DMSO-d_6). In both reaction sets, a new downfield peak was observed at 9.31 ppm in $CDCl_3$ upon mixing of **1a** or **1c** with $Pd(TFA)_2$. On the basis of shift, integration, and data from the analogous compounds **3a**, **3b**, and **4**, this peak was assigned to the N-bound Pd(II) species. This species was short-lived for the reaction with terminal alkene **1a** (Figure 5) but was persistent in the reaction with the internal alkene **1c**, suggesting that the initial cyclization is much faster for the terminal alkene. In the time-course experiment with **1c**, a downfield shift by 0.10 ppm of the alkene protons is observed,

Scheme 5. Plausible Mechanisms of Formation



and the new ^1H resonances integrate in a 1:1:1 ratio with the aryl proton peak at 9.31 ppm, suggesting the formation of a stable intermediate with palladium coordinated to the alkene, such as is seen with silver in complex **5**, and to the benzothiazole nitrogen (and not the thioether). Furthermore, at 1−3 h, novel peaks at 5.88 and 6.51 ppm for the reaction with **1a** in $CDCl_3$ and DMSO-d_6, respectively, are observed, consistent with the proposed cyclized intermediates. Similarly, the corresponding cyclic alkyl proton at the 1′-position in **6** (Figure 4) is significantly downfield at 5.58−5.51 ppm in DMSO-d_6.[21] Similar compounds, such as 2,3-dihydro[1,3]-thiazolo[2,3-*b*][1,3]benzothiazol-4-ium bromide,[24] also show downfield cyclic alkyl protons at around 5 ppm in DMSO-d_6.

Finally, in a series of preliminary C−C coupling experiments, we found that (±)-**2a** was a competent precatalyst for several reactions, including a Suzuki−Miyaura coupling, a Mizoroki−Heck reaction, and a dehydrogenative cross-coupling, when it was tested in air with conditions from the literature without further optimization (see Scheme S3 in the Supporting Information).

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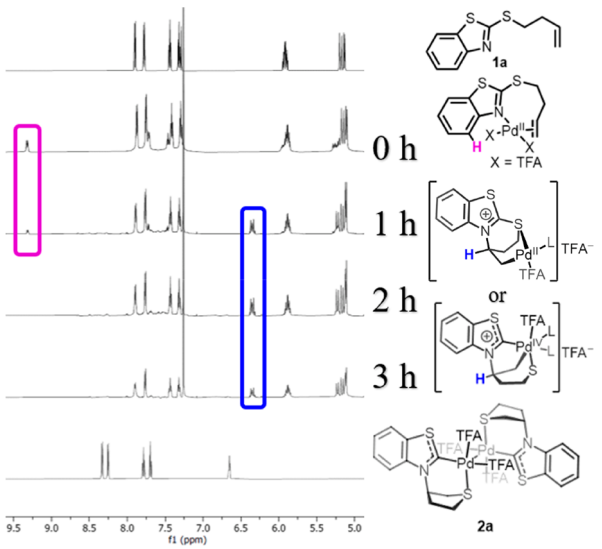

Figure 5. Time course of the reaction between **1a** and $Pd(TFA)_2$ to yield **2a**, taken in $CDCl_3$ with important new peaks highlighted. Full ^1H NMR spectra, precipitate analysis (DMSO-d_6), and the time course experiment with **1c** are available in the Supporting Information.

CONCLUSIONS

We have herein identified a novel rearrangement leading to tetrahydrothiophene-functionalized NSHC palladium(II) complexes. Using X-ray, NMR, and HRMS data, the identities of these [3.2.1]palladabicyclic products were confirmed. Through the synthesis of analogous complexes as well as the monitoring of the reaction progress of the formation of (±)-**2a** and (±)-**2c**, two plausible and closely related mechanisms can be proposed. Understanding this rearrangement process may bolster use of the benzo[*d*]thiazole directing group in catalytic alkene functionalization reactions. Additionally, (±)-**2a** can successfully catalyze three C−C coupling reactions, suggesting that complexes containing bidentate NSHC ligands can be developed and explored further as a new class of catalysts.

EXPERIMENTAL SECTION

General Information. Except where otherwise stated, all materials were used as received from commercial sources without further purification. All reactants, reagents, and solvents unless otherwise mentioned were purchased from Aldrich, Alfa Aesar, Oakwood, and Combi-Blocks and used without further drying or purification. All reactions were run in an atmosphere of air. NMR spectra were recorded on an AV-600 machine. Spectra were internally referenced to $SiMe_4$, the solvent signal, or an internal standard. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet. High-resolution mass spectra (HRMS) for new compounds were obtained with a Waters I-Class LC with diode array and G2-XS time-of-flight (TOF) mass spectrometer or with an Agilent LC/MSD TOF mass spectrometer.

Synthesis of Complexes (±)-2a−4. In a 1 dram (4 mL) vial equipped with a magnetic stir bar were placed the corresponding benzo[*d*]thiazole-containing material (0.2 mmol, 2 equiv) and the palladium-containing material (PdX_2) (0.1 mmol, 1 equiv). To this mixture was added 1,2-DCE (1 mL, 0.1 M), and the vial was capped. The reaction mixture was stirred at 500 rpm at 45 °C for 12 h. Without cooling to room temperature, the crude solution was transferred into a new 1 dram (4 mL) vial. This uncapped vial with the crude mixture was placed inside a scintillation vial (20 mL). Diethyl ether (2 mL) was placed in the scintillation vial without any addition into the 1 dram vial containing the crude material in preparation for vapor diffusion. The scintillation vial was capped and allowed to sit undisturbed for 72 h. The 1 dram vial was then removed from the scintillation vial and the solvent carefully removed with a pipet, leaving crystals, which were washed with additional diethyl ether (3 × 3 mL). The remaining diethyl ether was then removed *in vacuo* to provide the pure product.

*Complex (±)-**2a**.* The title compound was prepared with 2-(but-3-en-1-ylthio)benzo[*d*]thiazole (**1a**) and $Pd(TFA)_2$ on a 0.300 mmol scale. Purification afforded (±)-**2a** as a yellow crystal (137 mg, 41%). ^1H NMR (600 MHz, acetone-d_6): δ 8.33 (d, J = 8.6 Hz, 1H), 8.25 (dd, J = 8.1, 1.2 Hz, 1H), 7.79 (ddd, J = 8.5, 7.2, 1.2 Hz, 1H), 7.72−7.67 (m, 1H), 6.65 (t, J = 5.6 Hz, 1H), 4.14 (tt, J = 8.4, 5.0 Hz, 1H), 3.81 (d, J = 13.9 Hz, 1H), 3.51−3.42 (m, 2H), 3.12−3.03 (m, 1H), 2.89−2.84 (m, 1H). ^{13}C NMR (151 MHz, DMSO-d_6): δ 178.37, 142.99, 132.90, 127.91, 126.74, 123.18, 115.44, 66.23, 45.11, 41.96, 38.51, 34.19. HRMS: calcd for $C_{13}H_{11}F_3NO_2{}^{106}PdS_2{}^+$ [M/2 − TFA]$^+$, 439.9218; found, 439.9219. Single crystals suitable for X-ray diffraction were obtained directly from the procedure described above (CCDC 2057872).[28]

*Complex **2b**.* The title compound was prepared with 2-(pent-4-en-2-ylthio)benzo[*d*]thiazole (**1b**) and $Pd(TFA)_2$. Purification afforded **2b** as a yellow crystal (40 mg, 35%) with dr = 1.4:1 when (*S*)-2-(pent-4-en-2-ylthio)benzo[*d*]thiazole was used and dr = 1:3.3 when the racemic starting material was used. ^1H NMR (600 MHz, acetone-d_6): δ 8.31−8.23 (m, 2H), 7.78 (dtd, J = 8.5, 7.2, 1.2 Hz, 1H), 7.69 (ddt, J = 8.2, 7.2, 1.9 Hz, 1H), 6.65 (t, J = 4.9 Hz, 0.55H), 6.57 (t, J = 6.0 Hz, 0.42H), 4.85 (h, J = 7.2 Hz, 0.59H), 3.93 (dt, J = 9.2, 6.8 Hz, 0.45H), 3.81 (d, J = 14.2 Hz, 1H), 3.66 (dd, J = 14.1, 4.3 Hz, 0.55H), 3.59 (dd, J = 14.0, 4.8 Hz, 0.39H), 3.42−3.34 (m, 0.43H), 3.13−3.06 (m, 0.44H), 2.56 (ddd, J = 14.5, 7.2, 5.7 Hz, 0.50H), 2.40−2.32 (m, 0.45H), 1.97 (d, J = 6.8 Hz, 1.34H), 1.57 (d, J = 7.1 Hz, 1.67H). ^{13}C NMR (151 MHz, acetone-d_6): δ 181.37, 144.53, 144.32, 134.62, 128.84, 128.79, 127.66, 127.64, 123.91, 123.86, 115.88, 115.77, 69.20, 66.93, 53.24, 53.13, 44.47, 44.18, 42.96, 40.41, 21.67, 21.27. HRMS: calcd for $C_{14}H_{13}F_3NO_2{}^{102}PdS_2{}^+$ [M/2 − TFA]$^+$, 449.9396; found, 449.9388. Single crystals suitable for X-ray diffraction were obtained directly from the procedure described above (CCDC 2057870).[28]

*Complex (±)-**2c**.* The title compound was prepared with (*E*)-2-(hex-3-en-1-ylthio)benzo[*d*]thiazole ((*E*)-**1c**) and $Pd(TFA)_2$. Purification afforded (±)-**2c** as an orange crystal (43 mg, 37%). ^1H NMR (600 MHz, acetone-d_6): δ 8.39 (d, J = 8.6 Hz, 1H), 8.25 (dd, J = 8.1, 1.2 Hz, 1H), 7.77 (ddd, J = 8.5, 7.2, 1.2 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 6.35 (d, J = 6.4 Hz, 1H), 4.17−4.07 (m, 2H), 3.59 (ddd, J = 13.7, 10.7, 5.1 Hz, 1H), 3.17 (ddt, J = 14.8, 10.7, 6.0 Hz, 1H), 2.07−2.11 (m, 2H), 1.86 (ddq, J = 14.5, 9.7, 7.3 Hz, 1H), 1.21 (t, J = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, acetone-d_6): δ 180.18, 143.14, 132.90, 127.40, 126.27, 122.45, 116.55, 114.60, 114.26, 70.13, 60.09, 43.94, 36.08, 32.22, 29.24, 24.09, 11.12. HRMS: calcd for $C_{15}H_{15}F_3NO_2{}^{106}PdS_2{}^+$ [M/2 − TFA]$^+$, 467.9531; found, 467.9530. Single crystals with a triclinic structure suitable for X-ray diffraction were obtained directly from the procedure described above (CCDC 2057864)[28] and regrown in a trigonal structure from $CDCl_3$ (CCDC 2057865).[28]

*Complex (±)-**2d**.* The title compound was prepared with (*E*)-5-chloro-2-(hex-3-en-1-ylthio)benzo[*d*]thiazole (**1d**) and $Pd(TFA)_2$. Purification afforded (±)-**2d** as an orange crystal (45 mg, 36%). ^1H NMR (600 MHz, acetone-d_6): δ 8.57−8.49 (m, 1H), 8.27 (d, J = 8.6 Hz, 1H), 7.79−7.60 (m, 1H), 6.37 (d, J = 6.7 Hz, 1H), 4.22−4.06 (m, 2H), 3.72−3.52 (m, 1H), 3.25−3.08 (m, 1H), 2.94−2.86 (m, 1H), 2.26−2.06 (m, 1H), 1.86 (dddd, J = 17.6, 15.0, 8.4, 5.0 Hz, 1H), 1.20 (q, J = 8.1 Hz, 3H). ^{13}C NMR (151 MHz, acetone-d_6): δ 183.13, 144.60, 133.85, 132.15, 127.03, 124.14, 115.42, 115.13, 115.06, 70.98, 60.60, 44.42, 36.61, 32.65, 24.51, 11.59. HRMS: calcd for $C_{15}H_{14}{}^{35}ClF_3NO_2{}^{104}PdS_2{}^+$ [M/2 − TFA]$^+$, 499.9147; found, 499.9134. Single crystals suitable for X-ray diffraction were obtained directly from the procedure described above (CCDC 2057869).[28]

*Complex **3a**.* The title compound was prepared with 2-(but-3-en-1-ylthio)benzo[*d*]thiazole (**1a**) and $PdBr_2$. Purification afforded **3a** as a yellow crystal (33 mg, 46%). ^1H NMR (600 MHz, $CDCl_3$): δ 9.16

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(d, J = 8.3 Hz, 0.75H), 9.08 (d, J = 8.2 Hz, 0.25H), 7.71 (d, J = 7.9 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 5.99 (td, J = 16.9, 6.9 Hz, 1H), 5.40−5.11 (m, 2H), 3.50−3.38 (m, 2H), 2.86−2.70 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 174.35, 173.72, 150.39, 134.93, 134.86, 131.22, 131.11, 127.78, 125.72, 122.72, 122.62, 121.35, 121.26, 118.23, 118.06, 35.50, 35.45, 33.08, 32.96, 29.86. HRMS: calcd for $C_{22}H_{24}{}^{79}BrN_2{}^{106}PdS_4{}^+$ [M − Br + 2H]$^+$, 628.9041; found, 628.9022. Single crystals suitable for X-ray diffraction were obtained directly from the procedure described above (CCDC 2057868).[28]

Complex ***3b***. The title compound was prepared with 2-(but-3-en-1-ylthio)benzo[*d*]thiazole (**1a**) and $PdCl_2$. Crystals were regrown to X-ray quality by slow evaporation of $CDCl_3$ in an NMR tube. Purification afforded **3b** as a yellow crystal (32 mg, 51%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.26 (dt, J = 8.3, 0.9 Hz, 0.65H), 9.18 (dt, J = 8.2, 0.9 Hz, 0.35H), 7.76−7.71 (m, 1H), 7.68 (ddd, J = 8.4, 7.3, 1.2 Hz, 1H), 7.45 (dddd, J = 8.2, 7.2, 6.1, 1.1 Hz, 1H), 6.04−5.93 (m, 1H), 5.36−5.18 (m, 2H), 3.48−3.42 (m, 2H), 2.82−2.71 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 173.90, 173.27, 166.39, 152.87, 149.53, 135.26, 134.77, 134.33, 134.25, 130.67, 130.56, 127.32, 125.57, 125.16, 125.13, 123.73, 121.85, 121.70, 121.05, 120.77, 120.69, 120.50, 117.65, 117.48, 116.51, 34.82, 34.80, 32.90, 32.42, 32.30, 29.27. HRMS: calcd for $C_{22}H_{22}{}^{35}ClN_2{}^{106}PdS_4{}^+$ [M − Cl]$^+$, 582.9386; found, 582.9402. Single crystals suitable for X-ray diffraction were obtained directly from the procedure described above (CCDC 2051103).[28]

Complex ***4***. The title compound was prepared with 2-((2-methylbutyl)thio)benzo[*d*]thiazole (**1e**) and $Pd(TFA)_2$. Purification afforded **4** as an orange crystal (23 mg, 40%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.30 (dd, J = 11.2, 8.4 Hz, 1H), 7.70 (dq, J = 12.6, 8.8 Hz, 2H), 7.44 (t, J = 7.7 Hz, 1H), 3.37 (ddd, J = 13.1, 7.8, 5.9 Hz, 1H), 3.25−3.16 (m, 1H), 2.00 (qd, J = 13.7, 6.7 Hz, 1H), 1.68 (dtt, J = 13.0, 10.1, 6.3 Hz, 1H), 1.44 (dpd, J = 14.8, 7.4, 3.0 Hz, 1H), 1.19 (dd, J = 6.7, 4.2 Hz, 3H), 1.01 (q, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 176.59, 176.41, 149.81, 149.72, 130.54, 130.42, 128.08, 127.98, 125.81, 125.78, 122.02, 122.00, 121.18, 43.14, 43.04, 35.07, 35.01, 28.98, 28.94, 19.01, 11.37. HRMS: calcd for $C_{26}H_{30}F_3N_2O_2{}^{106}PdS_4{}^+$ [M − TFA]$^+$, 693.0177; found, 693.0168. Single crystals suitable for X-ray diffraction were obtained directly from the procedure described above (CCDC 2057871).[28]

Synthetic Procedure for Complex 5. In a 1 dram (4 mL) vial equipped with a magnetic stir bar were placed 2-(but-3-en-1-ylthio)benzo[*d*]thiazole (**1a**) (0.10 mmol, 2 equiv) and silver triflate (AgOTf) (0.05 mmol, 1 equiv). To this mixture was added 1,2-DCE (0.5 mL, 0.1 M), and the vial was capped. The reaction mixture was stirred at 500 rpm at 45 °C for 12 h. Without cooling to room temperature, the crude solution was transferred into a new 1 dram (4 mL) vial. This uncapped vial with the crude mixture was placed inside a scintillation vial (20 mL). Diethyl ether (2 mL) was placed in the scintillation vial without any addition into the 1 dram vial containing the crude material in preparation for vapor diffusion. The scintillation vial was capped and allowed to sit undisturbed for 72 h. The 1 dram vial was then removed from the scintillation vial and the solvent carefully removed with a pipet, leaving crystals, which were washed with additional diethyl ether (3 × 3 mL). The remaining diethyl ether was then removed *in vacuo* to provide the pure product **5** as a gray crystal (20 mg, 42%).

^{1}H NMR (600 MHz, acetone-d_6): δ 8.12 (dd, J = 15.3, 8.2 Hz, 2H), 7.59 (ddd, J = 8.3, 5.0, 1.3 Hz, 1H), 7.56−7.49 (m, 1H), 6.24 (ddtd, J = 13.4, 8.4, 6.7, 1.8 Hz, 1H), 5.45−5.36 (m, 2H), 3.71 (td, J = 6.5, 1.8 Hz, 2H), 2.75 (q, J = 6.7 Hz, 2H). ^{13}C NMR (151 MHz, acetone-d_6): δ 171.79, 152.45, 135.76, 134.98, 128.28, 126.71, 122.93, 122.63, 114.01, 36.68, 33.85. HRMS: calcd for $C_{11}H_{11}{}^{107}AgNS_2{}^+$ [M − OTf]$^+$, 327.9384; found, 327.9395. Single crystals suitable for X-ray diffraction were obtained directly from the procedure described above (CCDC 2057866).[28]

Synthetic Procedure for 4-(Iodomethyl)-3,4-dihydro-2*H*-benzo[4,5]thiazolo[2,3-*b*][1,3]thiazin-5-ium Triiodide (6). In a 1 dram (4 mL) vial equipped with a magnetic stir bar were placed 2-(but-3-en-1-ylthio)benzo[*d*]thiazole (**1a**) (0.5 mmol, 1 equiv) and samarium(II) iodide (SmI_2) (0.5 mmol, 0.1 M solution in THF, 1 equiv). To this mixture was added 1,2-DCE (5 mL, 0.1 M), and the vial was capped. The reaction mixture was stirred at 500 rpm at 45 °C for 12 h. Without cooling to room temperature, the crude solution was transferred into a new 1 dram (4 mL) vial. This uncapped vial with the crude mixture was placed inside a scintillation vial (20 mL). Diethyl ether (2 mL) was placed the scintillation vial without any addition into the 1 dram vial containing the crude material. The scintillation vial was capped and allowed to sit undisturbed for 72 h. The 1 dram vial was then removed from the scintillation vial and the solvent carefully removed with a pipet, leaving crystals, which were washed with additional diethyl ether (3 × 3 mL). The remaining diethyl ether was then removed *in vacuo* to provide the pure product. While some X-ray-quality crystals were retrievable, the yield of crystals was low (<10%). The reaction was rerun following a literature procedure.[21]

^{1}H NMR (600 MHz, DMSO-d_6): δ 8.32 (dt, J = 8.3, 2.0 Hz, 1H), 8.11 (dd, J = 8.6, 3.0 Hz, 1H), 7.86−7.78 (m, 1H), 7.71 (td, J = 7.7, 3.0 Hz, 1H), 5.54 (dh, J = 9.6, 3.1 Hz, 1H), 3.74−3.66 (m, 2H), 3.67−3.54 (m, 2H), 3.01 (dq, J = 15.1, 3.3 Hz, 1H), 2.46 (ddd, J = 15.5, 10.0, 4.3 Hz, 1H). ^{13}C NMR (151 MHz, DMSO): δ 175.83, 140.77, 128.69, 127.66, 127.09, 123.98, 114.96, 55.10, 23.25, 23.16, 2.10. Single crystals suitable for X-ray diffraction were obtained directly from the procedure described above (CCDC 2057863).[28]

Synthetic Procedure for [1,1′-Biphenyl]-4-carbaldehyde (7).[25] In a 1 dram (4 mL) vial equipped with a magnetic stir bar were placed 4-bromobenzaldehyde (0.3 mmol, 1 equiv), phenylboronic acid (0.36 mmol, 1.2 equiv), potassium carbonate (K_2CO_3) (1.0 mmol, 2 equiv), and (±)-**2a** (0.0015 mmol, 0.5 mol %). To this mixture was added a 1/1 mixture of H_2O and DMF (3 mL, 0.1 M). The vial was capped, placed on a preheated hot plate at 100 °C, and stirred at 500 rpm for 12 h. The reaction mixture was removed from the stir plate and cooled. The contents of the vial were transferred to a separation vial with subsequent washing of H_2O and EtOAc. Additional H_2O (50 mL) was placed in the separation vial, and the desired material was extracted with EtOAc (3 × 50 mL) and dried with Na_2SO_4. After the solvent was removed *in vacuo*, the crude residue was purified by SiO_2 gel column chromatography (5% EtOAc/95% hexanes). Purification afforded **7** as a white solid (90 mg, >95%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 10.06 (s, 1H), 7.95 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.49 (t, J = 7.8 Hz, 2H), 7.42 (t, J = 7.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 192.00, 147.24, 139.76, 135.27, 130.35, 129.10, 128.56, 127.75, 127.44.

Synthetic Procedure for (*E*)-4-(4-Methylstyryl)-benzaldehyde (8).[26] In a 1 dram (4 mL) vial equipped with a magnetic stir bar were placed the corresponding 4-bromobenzaldehyde (0.3 mmol, 1 equiv), 1-methyl-4-vinylbenzene (0.36 mmol, 1.2 equiv), potassium carbonate (K_2CO_3) (1.0 mmol, 2 equiv), and (±)-**2a** (0.0015 mmol, 0.5 mol %). To this mixture was added a 1/1 mixture of H_2O and DMF (3 mL, 0.1 M). The vial was capped, placed on a preheated hot plate at 100 °C, and stirred at 500 rpm for 12 h. The reaction mixture was removed from the stir plate and cooled. The contents of the vial were transferred to a separation vial with subsequent washing of H_2O and EtOAc. Additional H_2O (50 mL) was placed in the separation vial, and the desired material was extracted with EtOAc (3 × 50 mL) and dried with Na_2SO_4. After the solvent was removed *in vacuo*, the crude residue was purified by SiO_2 gel column chromatography (5% EtOAc/95% hexanes). Purification afforded **8** as a yellow solid (45 mg, 67%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 7.8 Hz, 2H), 7.27−7.19 (m, 3H), 7.10 (d, J = 16.2 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 191.79, 143.83, 138.77, 135.31, 133.93, 132.33, 130.40, 129.71, 126.99, 126.92, 126.47, 21.49.

Synthetic Procedure for 5-(Benzo[*d*]oxazol-2-yl)thiophene-2-carbaldehyde (9).[27] In a 1 dram (4 mL) vial equipped with a magnetic stir bar were placed benzo[*d*]oxazole (0.1 mmol, 1 equiv), thiophene-2-carbaldehyde (0.2 mmol, 2 equiv), silver acetate

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(AgOAc) (0.2 mmol, 2 equiv), and (±)-**2a** (0.05 mmol, 5 mol %). To this mixture was added a 1/1 mixtue of H_2O and DMSO (1 mL, 0.1 M). The vial was capped, placed on a preheated hot plate at 110 °C, and stirred at 500 rpm for 12 h. The reaction mixture was removed from the stir plate and cooled. The contents of the vial were transferred to a separation vial with subsequent washing of H_2O and EtOAc. Additional H_2O (50 mL) was placed the separation vial, and the desired material was extracted with EtOAc (3 × 50 mL) and dried with Na_2SO_4. After the solvent was removed *in vacuo*, the crude residue was purified by SiO_2 gel column chromatography (5% EtOAc/95% hexanes). Purification afforded **9** as a yellow solid (14 mg, 61%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 10.00 (d, J = 2.1 Hz, 1H), 7.97 (dd, J = 3.9, 2.1 Hz, 1H), 7.82 (dd, J = 4.0, 2.1 Hz, 1H), 7.79 (dt, J = 8.5, 1.7 Hz, 1H), 7.63−7.57 (m, 1H), 7.40 (pt, J = 7.4, 1.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 183.00, 157.81, 150.82, 146.39, 141.97, 137.78, 136.25, 130.04, 126.37, 125.41, 120.61, 110.93.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00041.

Experimental details, spectral data, NMR spectra, X-ray crystallographic data, and computational details (PDF)

NMR data (ZIP)

Accession Codes

CCDC 2051103 and 2057863−2057872 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing 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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The manuscript was written through contributions of all authors, and all authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

NHC, N-heterocyclic carbene; CAAC, cyclic (alkyl)- and (aryl)(amino)carbenes; *a*NHC, abnormal N-heterocyclic carbene; NXHC, N,X-heterocyclic carbene (X = O, P, S, etc.); $Pd(TFA)_2$, palladium(II) trifluoroacetate; 1,2-DCE, 1,2-dichloroethane; HRMS, high-resolution mass spectrometry; TFA, trifluoroacetate; AgOTf, silver(I) trifluoromethansulfonate; AgOAc, silver(I) acetate

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