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Benzimidazolin-2-ylidene Complexes of Palladium(II) Featuring a Thioether Moiety: Synthesis, Characterization, Molecular Dynamics, and Catalytic Activities

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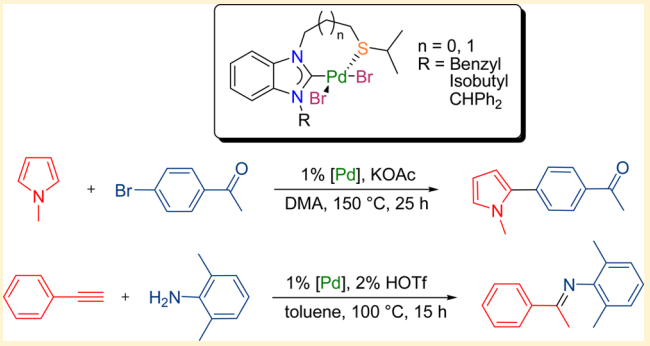
Supporting Information

ABSTRACT: Six benzimidazolin-2-ylidene palladium(II) complexes with an alkyl−alkyl thioether moiety in the side chain have been synthesized. Due to the hemilabile metal−sulfur bond, the complexes exhibit a marked fluxionality, as evidenced by NMR studies. The thioether moiety is readily displaced by pyridine as well as by another NHC ligand. Hetero(bis)-NHC complexes formally derived from all six chelating mono-NHC complexes have been synthesized as well. For both series of complexes, the catalytic activity has been explored, and they were found to be active catalysts for the intermolecular hydroamination reaction between a sterically hindered aniline and an alkyne in the presence of triflic acid. Furthermore, the complexes catalyze the direct arylation of 1-methylpyrrole.



INTRODUCTION

Complexes of late transition metals bearing N-heterocyclic carbene ligands have been tremendously successful during the past two decades, both as catalysts and for other applications.[1,2] The extraordinarily varied chemistry of this class of ligands can be attributed to their robustness and strong donating abilities, the relative ease with which they can be synthesized, and the various possibilities of fine-tuning their electronic and steric properties.[3] Additionally, the presence of side chains in close proximity to the metal center allows for the easy introduction of ancillary, tethered donor functionalities, which gives rise to chelating and pincer-type ligands with interesting properties.[4] Besides functionalities based on oxygen,[5] nitrogen,[6] or phosphorus,[7] there has been an increasing interest in sulfur-based donor moieties as well. These include functionalities as diverse as thiolates, thioethers, thiophenes, and sulfoxides.[8,9] Especially thioethers have emerged as a useful functionality in the side chain of NHC ligands due to their potentially hemilabile behavior. The metal-sulfur bond is weak enough to allow for the rapid opening up of free coordination sites at the metal center during catalysis, while being sufficiently strong to stabilize the catalyst in its resting state.[10]

Recently, we reported the synthesis and catalytic activities of a series of platinum(II) complexes with alkyl−alkyl thioether-functionalized benzimidazolin-2-ylidene ligands.[11] Due to the relatively harder nature of palladium(II), a pronounced hemilabile behavior is to be expected for this metal.[12] Furthermore, there is a close structural relationship with other sulfur-functionalized palladium(II) NHC complexes, which were previously prepared in our lab. This prompted us to expand our chemistry and explore the coordination chemistry of our thioether-functionalized NHCs with palladium(II) as well as the catalytic properties of the resulting complexes.

RESULTS AND DISCUSSION

Complex Synthesis. Similarly to the synthesis of their platinum(II) analogues, the palladium(II) complexes were prepared by silver carbene transfer.[11,13] The corresponding silver(I) complexes for the previously described ligand precursors with ethylene (**1**−**3**) and propylene (**7**−**9**) thioether tethers were obtained by reaction with silver(I) oxide in dichloromethane and directly added to a freshly prepared solution of $[PdBr_2(MeCN)_2]$ in acetonitrile. The instantaneous precipitation of insoluble silver(I) bromide indicated rapid transmetalation, and the desired palladium complexes **4**−**6** and **10**−**12** could be isolated from the reaction mixture in good to excellent yields (Scheme 1).

The complexes were obtained as microcrystalline, yellow solids. All complexes are completely insoluble in hydrocarbons and ethereal solvents and only sparingly soluble in chlorinated solvents and polar organic solvents such as DMSO. In the presence of small amounts of coordinating solvents such as pyridine, the solubility in polar organic solvents and chlorinated solvents increases markedly, due to the formation of solvent

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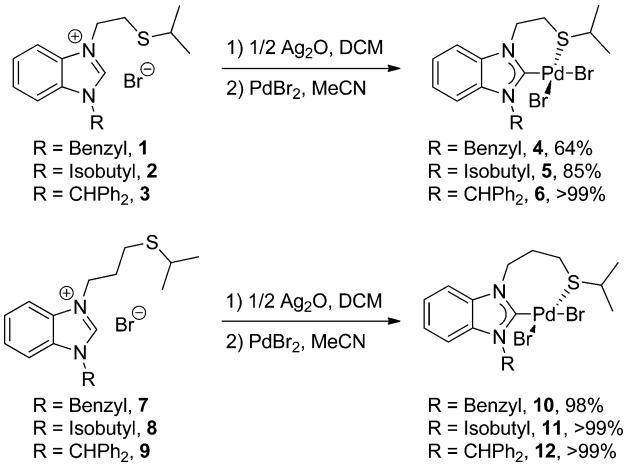
Scheme 1. Synthesis of Thioether-Functionalized Palladium(II) NHC Complexes



adducts by displacement of the weakly coordinated thioether moiety.

The characterization of these complexes by means of NMR spectroscopy was challenging due to their low solubility and their dynamic behavior (vide infra). However, the complexes were unambiguously characterized by mass spectrometry, elemental analysis, and in some cases X-ray crystallography.

Since the thioether moiety is only weakly bound to the metal center, it is readily displaced by stronger donor ligands such as nitrogen, phosphorus, or carbon donors. This was demonstrated by the synthesis of a second series of complexes, which incorporate two different benzimidazolin-2-ylidene ligands and a pendant thioether side chain. For the synthesis of these hetero(bis)-NHC complexes, two routes are possible (Scheme 2). They can be synthesized either by the transmetalation reaction of complexes **4**–**6** and **10**–**12** with one equivalent of in situ prepared [AgBr(^{i}Pr$_2$-bimy] (^{i}Pr$_2$-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene) or by bridge-cleavage reaction of [PdBr$_2$(^{i}Pr$_2$-bimy)]$_2$ with silver(I) complexes of the thioether-NHC ligands.

Both methods lead to the formation of the desired complexes **13**–**18**. However, the reaction with [PdBr$_2$(^{i}Pr$_2$-bimy)]$_2$ is more attractive, since all six complexes can be synthesized by a single-step reaction from a common precursor, while the inverted approach requires the synthesis of each individual mono-NHC κ^2*C*,*S* complex **4**–**6** and **10**–**12** first, followed by the silver carbene transfer of the ^{i}Pr$_2$-bimy ligand. Additionally, the reaction between dimeric [PdBr$_2$(^{i}Pr$_2$-bimy)]$_2$ and the respective silver(I) carbene complexes was found to proceed cleaner and considerably faster than the reactions between the κ^2*C*,*S* complexes and [AgBr(^{i}Pr$_2$-bimy], which were accompanied by the formation of byproducts arising from ligand scrambling.

All bis-NHC complexes were obtained in good yields as yellow solids with a markedly higher solubility than their mono-NHC counterparts. While being fully soluble in chlorinated solvents as well as polar organics solvents, they are not soluble in ethereal solvents and hydrocarbons. The complexes were fully characterized by NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray crystallography.

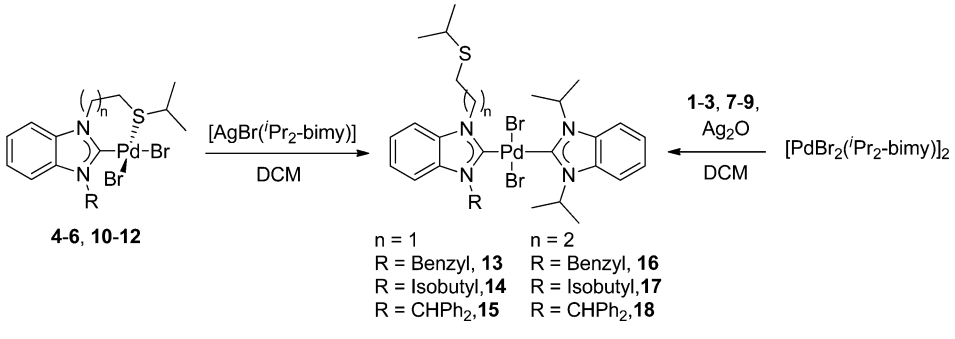
Dynamic Behavior and NMR Spectroscopy. The chelate complexes **4**–**6** and **10**–**12** are only sparingly soluble in common deuterated solvents, making the measurement of NMR spectra difficult. Additionally, all complexes show dynamic behavior, resulting in considerable signal broadening in their NMR spectra due to a coalescence temperature close to ambient temperature. Especially the signals of the thioether side chains are affected by this phenomenon, and in most cases some of the protons in the side chain cannot be observed at all. Measurements at low temperature are impossible, because of solubility problems, but high-temperature measurements up to 368 K were conducted as illustrated for complex **4** in Figure 1.

At ambient temperature, the methylene protons of the thioether side chain could barely be observed due to peak broadening, and no signal for the methine proton in the side chain was detected at all. These signals were clearly observed at elevated temperatures. By lowering the temperature back to ambient temperature, the initial spectrum could be restored. However, **4** was the only compound for which coalescence could be observed, while the other complexes showed no coalescence before decomposition in solution occurred.

To circumvent the problems arising from the fluxional behavior due to the weak coordination of the thioether moiety and the low solubility of these complexes, the complexes were reacted with pyridine in dichloromethane. Clean pyridine adducts were obtained for the ethylene-linked complexes **4**–**6**, while the propylene-linked complexes **10**–**12** gave a mixture of the desired pyridine adducts and other, unidentified species. Attempts at separating these complex mixtures were futile, since they rapidly re-equilibrated.

The pyridine adducts of **4**–**6** were readily soluble in chlorinated solvents, so NMR spectra could be measured in deuterated chloroform. Upon introduction of an additional donor ligand to the complex, no more dynamic behavior was observed, and the spectra show sharp multiplets attributable to the protons in the side chain. These marked changes confirm an initial κ^2*C*,*S* coordination mode, which is not feasible if the

Scheme 2. Possible Approaches for the Preparation of Palladium(II) Bis-NHC Complexes



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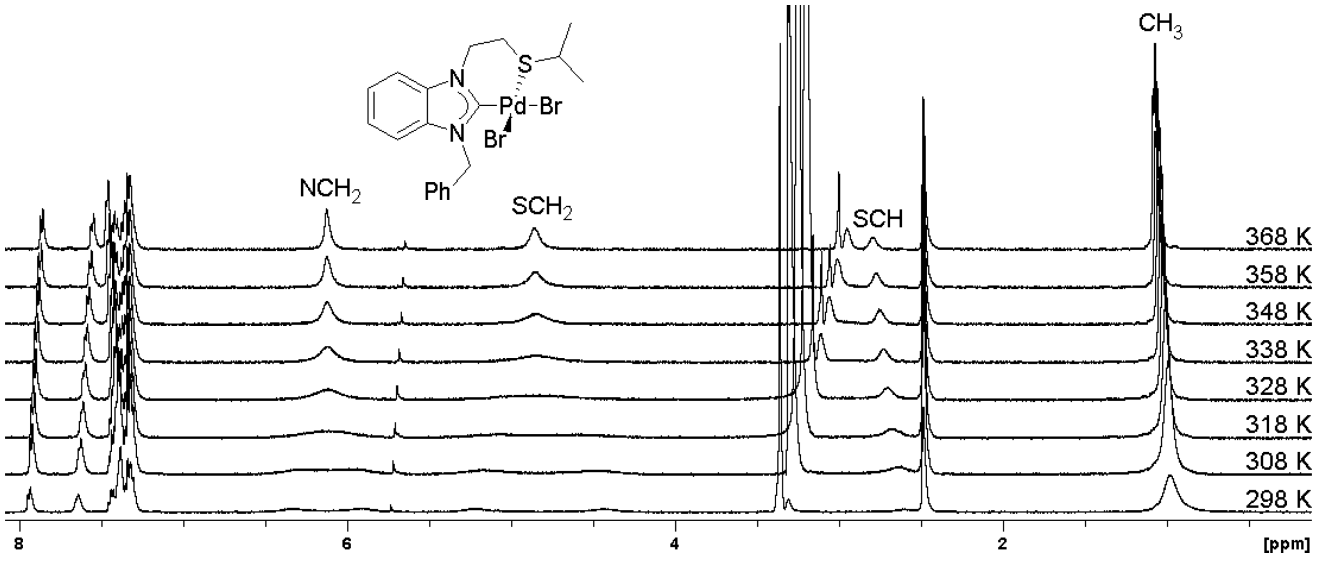

Figure 1. Variable-temperature ^{1}H NMR spectra of **4** in DMSO-d_6.

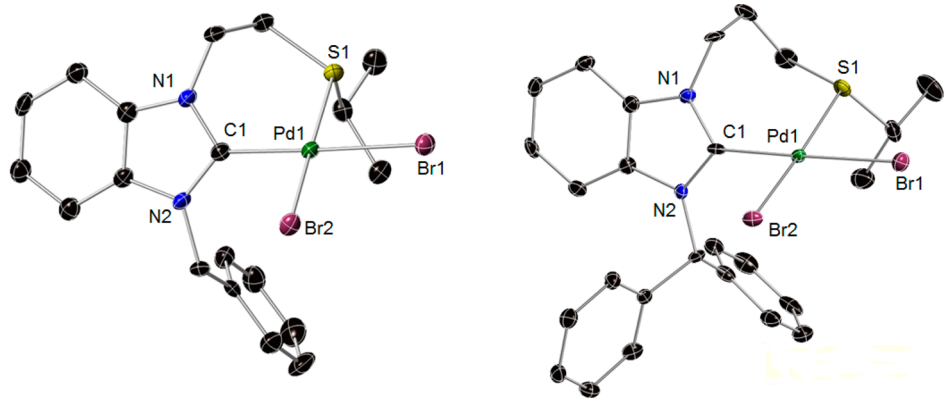

Figure 2. Molecular structures of **4** and **12**. Thermal ellipsoids are shown at 50% probability; hydrogen atoms have been omitted for clarity.

coordination site is blocked by the pyridine ligand. NCH_2 groups are observed as a multiplet between 5.13 and 4.97 ppm, SCH_2 as a multiplet between 3.47 and 3.33 ppm, SCH either as a multiplet or as a septet between 3.26 and 3.06 ppm, and the CH_3 groups as a doublet at ∼1.40 ppm. These values are slightly downfield from those observed for the salt precursors **1**−**3**. In the spectra of all pyridine adducts, the identity as NHC complexes is confirmed by the absence of the characteristic signals of the acidic proton on C2 in the ligand precursor salts. In their ^{13}C NMR spectra, the $C_{carbene}$ atoms resonate at 163−166 ppm, which is in good agreement with reported values for similar complexes.[14]

The spectroscopic characterization of the hetero(bis)-NHC complexes **13**−**18** was more straightforward. In the ^{1}H NMR spectra, the disappearance of the acidic proton present in the precursor salts indicated successful formation of a carbene complex. In **13**−**15**, the sharp signals observed for the thioether side chain are almost identical to the signals found for the pyridine adducts of **4**−**6**. For **16**−**18**, the signals for SCH_2 groups are found more upfield at 2.87−2.80 ppm as a well-resolved triplet, while the septets attributable to the SCH groups are found further upfield at 3.16−3.02 ppm. The additional CH_2 group in the propylene linker gives rise to multiplets at 2.71−2.60 ppm. Due to the asymmetry of the thioether-functionalized benzimidazolin-2-ylidenes and the hindered rotation along the metal−carbon bonds, the isopropyl groups of the $^{i}Pr_2$-bimy ligands experience a different environment, which results in two distinct signal sets for these functionalities.

In their ^{13}C NMR spectra, two carbene signals are observed for each complex. The resonances attributable to the $^{i}Pr_2$-bimy ligand fall within the narrow range of 178.6−179.6 ppm, while those for the sulfur-functionalized benzimidazolin-2-ylidene ligands range from 183.5 to 186.3 ppm. These values are in line with previously reported chemical shifts for similar complexes.[15] The nature of the thioether side chain has a smaller impact on these shifts than the nonfunctionalized side chain, reflecting the negligible influence of linker length on the electronic properties of the complex.

Molecular Structures. The slow evaporation of concentrated solutions yielded single crystals suitable for X-ray diffraction analysis for several complexes (**13**, **14**, and **18** from dichloromethane/acetonitrile, **5** from pure dichloromethane, **6** from dichloromethane/toluene, **12** from acetonitrile/hexane, **16** from dichloromethane/hexane). The slow diffusion of diethyl ether in a concentrated dichloromethane solution of **4** yielded single crystals, and crystals of **16** were obtained by slow diffusion of hexane into a concentrated dichloromethane solution. Despite numerous attempts, no single crystals could be obtained for **10**, **11**, and **17**. A likely

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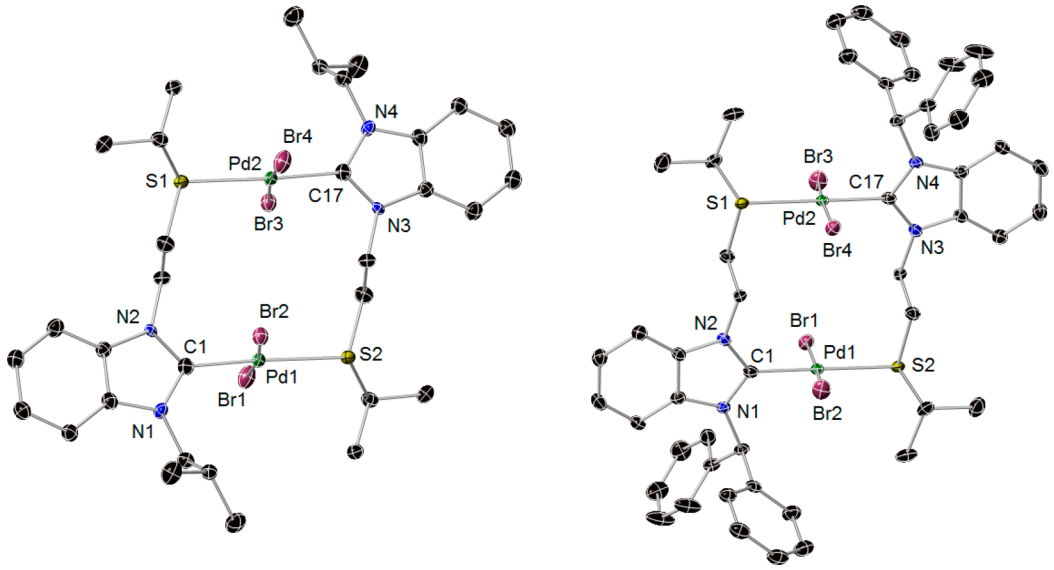

Figure 3. Molecular structures of **5** and **6**. Thermal ellipsoids are shown at 50% probability; hydrogen atoms and solvent molecules have been omitted for clarity.

reason is the flexibility of the long, aliphatic side chains found in these complexes, which prevents an efficient crystal packing.

Interestingly, not all mono-NHC complexes showed the expected κ^2C,S coordination in the solid state. While **4** and **12** crystallized as mononuclear complexes, **5** and **6** were found to adopt a dimeric form, in which the thioether moiety and $C_{carbene}$ coordinate to different metal centers, forming a 12-membered macrocycle (Figures 2 and 3). Similar species were proposed to occur in solution as part of dynamic equilibria for related platinum(II) and palladium(II) complexes,[9b,11] and multiple coordination modes are not uncommon for sulfur-functionalized palladium(II) complexes.[8c,d,h,10c,16]

The metallacycles in the chelating complexes **4** and **12** adopt a mildly distorted boat conformation. The plane defined by the NHC ring and the coordination plane are twisted by 44.0(3)° with respect to each other in complex **4**, while the longer propylene linker in **12** allows for a higher degree of conformational freedom, and thus a larger twist of 58.0(5)° can be found. In both cases, the coordination geometry around the palladium center is distorted square planar. The Pd−C bond in **4** has a length of 1.974(3) Å. In **12**, it is slightly longer at 1.993(5) Å. The Pd−S distances are 2.2955(9) and 2.296(1) Å, respectively.

The two different Pd−Br bonds show a marked difference, reflecting the difference in *trans* influence between the weakly donating thioether moiety and the NHC. The bond *trans* to the carbene is 2.4739(6) Å long in complex **4** and 2.4799(7) Å in complex **12**, and the bond distance between palladium and the bromido ligand *trans* to the thioether is 2.4392(5) Å in **4** and 2.4431(7) Å in **12**.

The bond lengths are in good agreement with values reported for similar chelate complexes (Table 1).[9b,10c]

In contrast to the κ^2C,S chelates **4** and **12**, complexes **5** and **6** were found to crystallize preferentially in a *trans*-coordinated, dimeric form. In both complexes, the coordination geometry around the palladium centers is distorted square planar. Bond lengths fall well within the expected range, based on comparison with similar compounds (Table 2).[8c] When compared to the two κ^2C,S complexes, the Pd−C bonds are shorter with a length of 1.95(1) Å in **5** and 1.964(2) Å in **6**. In contrast, the Pd−S bonds are elongated with a length of 2.379(3) Å in **5** and 2.3791(6) Å in **6**. Again, these changes are brought about by the difference in *trans* influence of the opposing ligand. The Pd−Br bond lengths fall in between the extremes realized in the κ^2C,S complexes, with values in the range from 2.4189(3) to 2.434(2) Å.

While the dimeric form seems to be preferred in the solid state for these two compounds, only compound **6** showed the peaks corresponding to the dimeric form in ESI mass spectrometry. For complex **5**, the monomeric form was observed instead.

Table 1. Bond Distances (Å) and Angles (deg) in Complexes 4 and 12

bond parameter	4	12
Pd1−C1	1.974(3)	1.993(5)
Pd1−S1	2.2955(9)	2.296(1)
Pd1−Br1	2.4739(6)	2.4799(7)
Pd1−Br2	2.4392(5)	2.4431(7)
C1−Pd1−S1	90.9(1)	94.1(2)
C1−Pd1−Br2	92.39(9)	88.0(2)
S1−Pd1−Br1	85.57(2)	85.21(4)
Br1−Pd1−Br2	91.22(1)	92.61(2)
C1−Pd1−Br1	176.33(9)	178.9(2)
S1−Pd1−Br2	173.81(3)	172.93(4)

Table 2. Bond Distances (Å) and Angles (deg) in Complexes 5 and 6

bond parameter	5	6
Pd1−C1	1.95(1)	1.964(2)
Pd1−S2	2.379(3)	2.3791(6)
Pd1−Br1	2.434(2)	2.4308(3)
Pd1−Br2	2.427(2)	2.4189(3)
C1−Pd1−Br1	89.6(3)	89.08(7)
C1−Pd1−Br2	85.0(3)	86.31(7)
S2−Pd1−Br1	86.80(9)	89.88(2)
S2−Pd1−Br2	98.93(9)	94.78(2)
C1−Pd1−S2	174.1(3)	178.77(7)
Br1−Pd1−Br2	173.27(6)	173.13(1)

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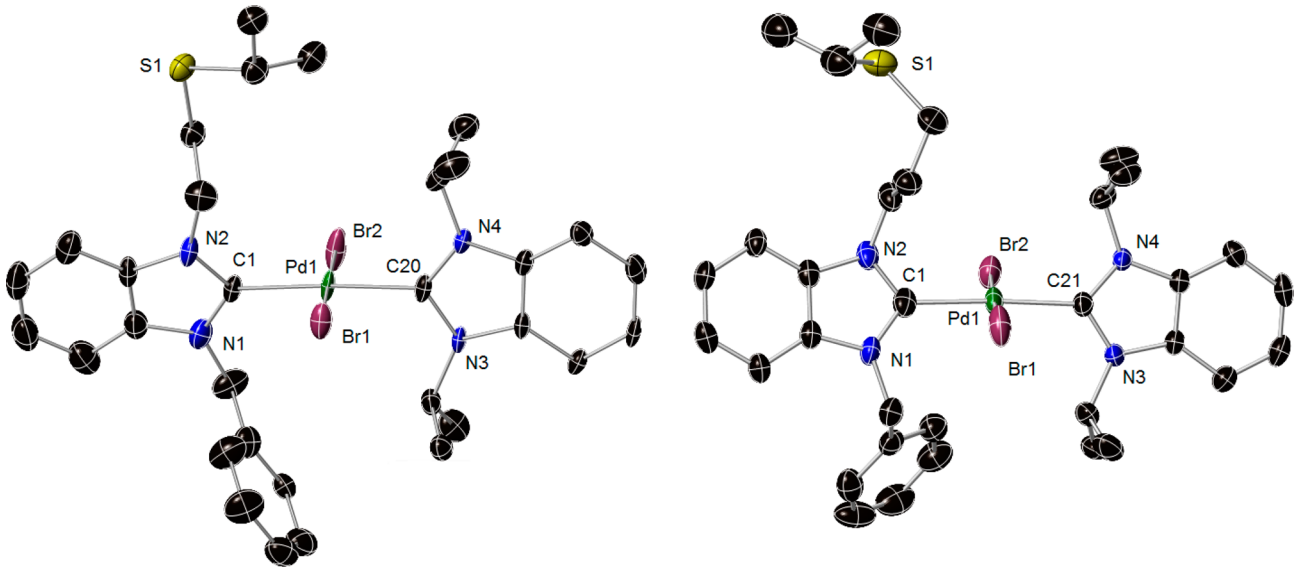

Figure 4. Molecular structures of **13** and **16**. Thermal ellipsoids are shown at 50% probability; hydrogen atoms and disordered atoms in the thioether side chain have been omitted for clarity.

The hetero(bis)-NHC complexes **13**–**16** and **18** adopt a square planar coordination geometry at the metal center, with a *trans* arrangement of the two different benzimidazolin-2-ylidene ligands (Figures 4–6). With the exception of **14**, all molecular structures showed disordering of the long and flexible thioether side chain. The Pd–C bonds are between 2.011(5) and 2.040(4) Å long. For the Pd–Br bonds, values ranging from 2.440(2) to 2.4567(9) Å are found. Only minor differences exist between the complexes, and the bond lengths are close to those typically found for such hetero(bis)-NHC complexes (Table 3).[15a,17]

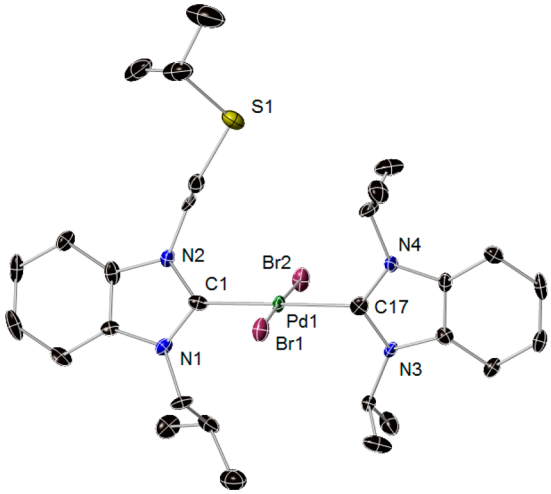

Figure 5. Molecular structure of **14**. Thermal ellipsoids are shown at 50% probability; hydrogen atoms have been omitted for clarity.

Hydroamination of Phenylacteylene. The hydroamination reaction of alkynes and alkenes is an important strategy for the formation of carbon–nitrogen bonds.[18] The direct addition of primary and secondary amines to carbon–carbon multiple bonds proceeds with perfect atom economy and avoids the formation of wasteful byproducts, thus following central tenets of green chemistry. Several late transition metal NHC complexes were found to be efficient catalysts for this kind of transformation,[19] including several palladium(II) NHC complexes.[20]

In light of our recent experiences with sulfur-functionalized NHC complexes of group 10 metals as catalysts for hydroaminations of alkynes,[9e,11] the catalytic performance of complexes **4**–**6**, **10**–**12**, and **13**–**18** in the reaction between phenylacetylene (**19**) and 2,6-dimethylaniline (**20**) was explored. In the absence of any additive, only low to moderate yields were achieved when using the κ^2C,S as catalysts, and no clear trends were discernible. The highest yield was obtained with complex **10** (entry 5, Table 4). Considerably higher yields were obtained in the presence of a catalytic amount of triflic acid, which likely speeds up the protolytic cleavage of the metal–carbon bond formed after the nucleophilic attack of the amine.[21] Yields were moderate to good for the κ^2C,S complexes and moderate for the corresponding hetero(bis)-NHC complexes. The best catalytic performance was found for the chelating complexes **4** and **5**, which feature a stable six-membered metallacycle. A likely reason could be a prolonged catalyst lifetime due to the more efficient stabilization of the catalytically active species by the hemilabile thioether moiety.

By contrast, the hetero(bis)-NHC complexes **13**–**18** were almost in all cases less efficient than their mono-NHC counterparts. A plausible reason is the slower formation of the catalytically active species, since the additional NHC ligand blocks a coordination site.

Direct Arylation of 1-Methylpyrrole. In contrast to classical carbon–carbon cross-coupling reactions, which require the use of organometallic reagents as precursors, direct arylation reactions allow the synthesis of biaryls starting from halidoarenes and electron-poor polyfluoroarenes or heteroarenes by C–H activation.[22] The direct arylation of 1-methylpyrrole has attracted considerable interest, and palladium NHC complexes have recently been shown to catalyze this reaction in good yields.[23] Using reaction conditions described in the literature, all complexes were evaluated for their ability to act as catalysts in the reaction between 1-methylpyrrole (**22**) and 4-bromoacetophenone (**23**). All

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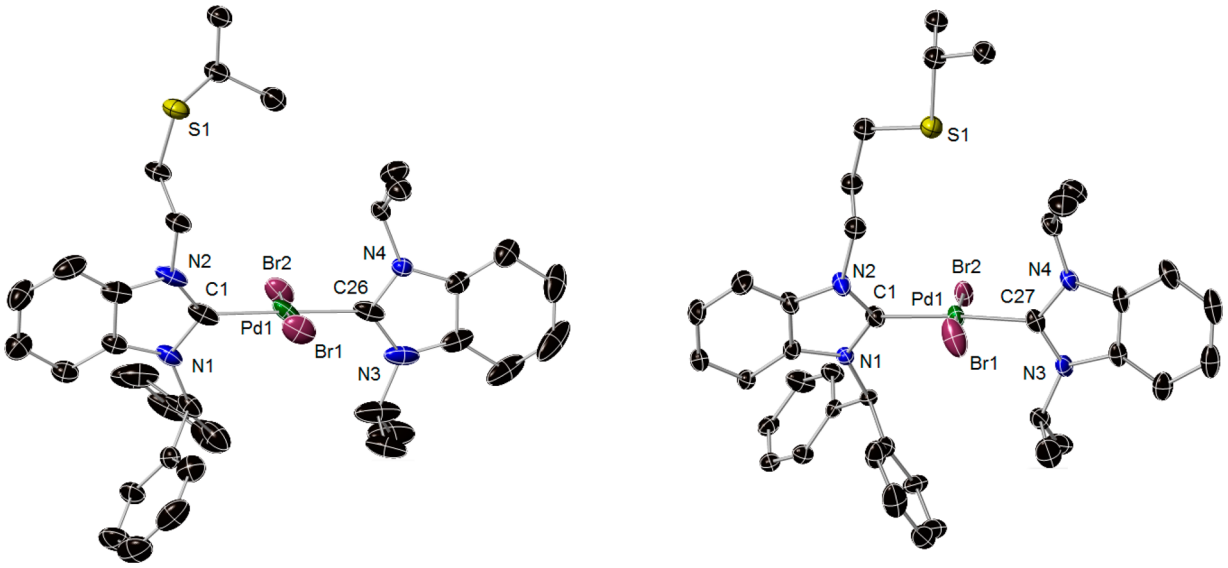


Figure 6. Molecular structures of **15** and **18**. Thermal ellipsoids are shown at 50% probability; hydrogen atoms, disordered atoms in the thioether side chain, and solvent molecules have been omitted for clarity.

Table 3. Bond Distances (Å) and Angles (deg) in Complexes 13−16 and 18

bond parameter	13	14	15	16	18
Pd1−C1	2.031(7)	2.013(8)	2.029(5)	2.031(4)	2.040(4)
Pd1−C	2.027(7)	2.023(8)	2.011(5)	2.021(3)	2.01(2)
Pd1−Br1	2.443(2)	2.456(2)	2.443(1)	2.4567(9)	2.4451(5)
Pd1−Br2	2.440(2)	2.453(2)	2.447(1)	2.4383(9)	2.4262(6)
C1−Pd1−Br1	90.9(2)	90.2(3)	91.9(9)	92.0(1)	94.3(1)
C1−Pd1−Br2	89.9(2)	92.5(3)	91.0(1)	88.9(1)	89.4(1)
C−Pd1−Br1	89.1(2)	89.4(3)	89.5(1)	89.3(1)	89.7(1)
C−Pd1−Br2	90.1(2)	87.9(3)	87.6(1)	89.8(1)	86.5(1)
C1−Pd1−C	176.6(2)	179.5(4)	178.4(2)	176.8(2)	174.8(2)
Br1−Pd1−Br1	178.94(3)	177.17(5)	176.63(3)	177.78(2)	176.19(2)

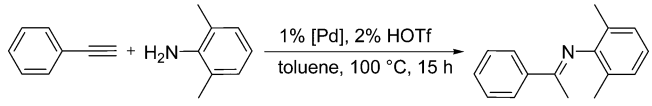
Table 4. Catalyst Performance in the Hydroamination of Phenylacetylene[a]

		yield (%)[b]	
entry	catalyst	no additive	+ 2% HOTf
1		0	0
2	**4**	20	88
3	**5**	34	78
4	**6**	51	56
5	**10**	53	53
6	**11**	29	38
7	**12**	48	58
8	**13**		37
9	**14**		46
10	**15**		60
11	**16**		51
12	**17**		55
13	**18**		51

[a]Reaction conditions: 1 mol % precatalyst, phenylacetylene (2.0 equiv), 2,6-dimethylaniline (1.0 mmol), toluene (3 mL), 100 °C, 15 h. [b]Yields determined by GC-MS with decane as internal standard; average of two runs.

complexes were found to be active catalysts, and good yields of the desired product were obtained (Table 5).

Scheme 3. Hydroamination of Phenylacetylene with 2,6-Dimethylaniline



There was only a minor variation in yield between the different complexes under scrutiny, possibly because of partial catalyst decomposition and the involvement of colloidal palladium in the catalysis.

For the κ^2C,S complexes, no significant difference was found between complexes **4**−**6** featuring an ethylene linker and complexes **10**−**12** featuring a propylene linker between the carbene and the thioether moieties. However, catalyst performance depends on the sterical bulk of the noncoordinating side chain. The highest yields were obtained with complexes featuring the bulky benzhydryl side chain, which might favor the reductive elimination step in the catalytic cycle.[24]

A similar pattern was observed for the hetero(bis)-NHC complexes: only minor changes due to the different linker lengths between carbene and thioether moieties, and better results with bulkier noncoordinating side chains. In general, the hetero(bis)-NHC complexes performed slightly better than

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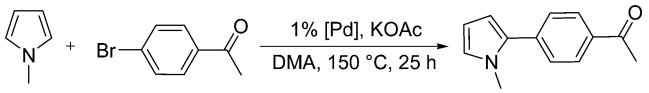
Table 5. Catalyst Performance in the Direct Arylation of 1-Methylpyrrole[a]

entry	catalyst	yield (%)[b]
1		0
2	**4**	69
3	**5**	75
4	**6**	80
5	**10**	67
6	**11**	74
7	**12**	77
8	**13**	74
9	**14**	77
10	**15**	83
11	**16**	71
12	**17**	66
13	**18**	86

[a]Reaction conditions: 1 mol % precatalyst, 1-methylpyrrole (4.0 equiv), 4-bromoacetophenone (1.0 mmol), KOAc (2.0 equiv), DMA (3 mL), 150 °C, 20 h. [b]Yields determined by GC-MS with decane as internal standard; average of two runs.

their κ^2C,S counterparts presumably due to a higher stability under the harsh reaction conditions.

Scheme 4. Direct Arylation of 1-Methylpyrrole



22 **23** **24**

CONCLUSION

A series of six thioether-functionalized κ^2C,S palladium(II) NHC complexes has been synthesized. Characterization by NMR spectroscopy proved difficult due to the marked hemilabile behavior of the thioether moieties. X-ray crystallography revealed the existence of two different coordination modes, thus providing the first direct evidence for previously postulated species. The thioether moieties were readily replaced by other donor ligands, and a series of hetero(bis)-NHC complexes, formally derived from the κ^2C,S complexes, has been synthesized as well.

Both series of complexes were found to be catalytically active in the hydroamination of phenylacetylene, although good yields were obtained only in the presence of triflic acid. For all complexes, a consistently good catalytic performance was observed in the direct arylation of 1-methylpyrrole, and future work will focus on other similar direct arylation reactions.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out without precautions to exclude air and moisture, unless stated otherwise. All solvents and chemicals were used as received or dried using standard procedures when appropriate. NMR spectra were recorded on either a 300 MHz or a 500 MHz spectrometer. The chemical shifts (δ) were internally referenced to the residual solvent signals relative to tetramethylsilane (^{1}H, ^{13}C). Melting points were determined in open capillaries. Elemental analyses were performed at the Department of Chemistry, National University of Singapore. The ligand precursors **1**–**3** and **7**–**9**[11] as well as $[PdBr_2(^iPr_2\text{-bimy})]_2$[25] were prepared following established procedures.

*cis-Dibromido(1-benzyl-3-(2-(isopropylthio)ethyl)-benzimidazolin-2-ylidene-κ^2C,S)palladium(II) (**4**).* Salt **1** (117 mg, 0.30 mmol, 1.00 equiv) and silver(I) oxide (35 mg, 0.15 mmol, 0.50 equiv) were suspended in dichloromethane (15 mL) and stirred at ambient temperature for 15 h shielded from light. Palladium(II) bromide (80 mg, 0.30 mmol, 1.00 equiv) was dissolved in acetonitrile (10 mL) by stirring for 30 min at 50 °C. After cooling to ambient temperature, the silver carbene complex solution was added by filtration over a short plug of Celite, and stirring was continued for 1 h at ambient temperature. Then the solution was filtered over Celite and the solvent was removed under reduced pressure. The residue was washed with diethyl ether (10 mL). The product was obtained as a yellow solid (111 mg, 0.19 mmol, 64%). ^{1}H NMR (300 MHz, DMSO-d_6, 358 K): δ 7.87 (d, $^3J_{H-H}$ = 8 Hz, 1 H, Ar–H), 7.56 (d, $^3J_{H-H}$ = 8 Hz, 1 H, Ar–H), 7.49–7.25 (m, 9 H, Ar–H, NCH_2Ph), 6.19–6.05 (m, 2 H, NCH_2), 4.98–4.72 (m, 2 H, SCH_2), 2.85–2.73 (m, 1 H, SCH), 1.09–1.02 (m, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6): δ 136.4, 134.4, 133.3, 129.1, 128.4, 127.9, 124.6, 124.4, 112.3 (Ar–C), 51.6 (NCH_2Ph), 47.2 (NCH_2), 44.3 (SCH), 30.8 (SCH_2), 22.6 (CH_3), $C_{carbene}$ not observed. ^{1}H NMR (300 MHz, $CDCl_3$, as pyridine adduct): δ 9.06–8.99 (m, 2 H, Ar–H), 7.81–7.77 (m, 1 H, Ar–H), 7.60–7.52 (m, 2 H, Ar–H), 7.47–7.42 (m, 1 H, Ar–H), 7.38–7.30 (m, 5 H, Ar–H), 7.25–7.21 (m, 1 H, Ar–H), 7.14–7.01 (m, 2 H, Ar–H), 6.16 (s, 2 H, NCH_2Ph), 5.11–5.01 (m, 2 H, NCH_2), 3.47–3.34 (m, 2 H, SCH_2), 3.22 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, CH), 1.41 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, as pyridine adduct): δ 164.2 ($C_{carbene}$), 153.2, 138.7, 135.4, 135.4, 134.9, 129.5, 128.9, 128.8, 125.3, 123.9, 123.9, 112.3, 110.9 (Ar–C), 54.3 (NCH_2Ph), 49.6 (NCH_2), 36.1 (SCH), 29.6 (SCH_2), 24.5 (CH_3). Mp: 204 °C (dec). Anal. Calcd for $C_{19}H_{22}Br_2N_2PdS$: C, 39.57; H, 3.85; N, 4.86. Found: C, 39.45; H, 3.89; N, 4.85. MS (ESI): m/z 497 $[M - Br]^+$.

*cis-Dibromido(1-isobutyl-3-(2-(isopropylthio)ethyl)-benzimidazolin-2-ylidene-κ^2C,S)palladium(II) (**5**).* The compound was prepared in analogy to **4** from **2** (107 mg, 0.30 mmol, 1.00 equiv), silver(I) oxide (35 mg, 0.15 mmol, 0.50 equiv), and palladium(II) bromide (80 mg, 0.30 mmol, 1.00 equiv). The product was obtained as a yellow solid (139 mg, 0.26 mmol, 85%). ^{1}H NMR (300 MHz, $CDCl_3$, as pyridine adduct): δ 9.08–8.97 (m, 2 H, Ar–H), 7.85–7.74 (m, 1 H, Ar–H), 7.49–7.34 (m, 4 H, Ar–H), 7.33–7.26 (m, 2 H, Ar–H), 5.10–4.97 (m, 2 H, NCH_2), 4.55 (d, $^3J_{H-H}$ = 8 Hz, 2 H, NCH_2), 3.42–3.30 (m, 2 H, SCH_2), 3.26–3.06 (m, 2 H, SCH, CH), 1.39 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3), 1.11 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, as pyridine adduct): δ 163.3 ($C_{carbene}$), 153.2, 138.7, 136.1, 134.8, 125.3, 123.8, 111.5, 110.9 (Ar–C), 56.7 (NCH_2), 49.7 (NCH_2), 36.1 (SCH), 29.8 (SCH_2), 29.6 (CH), 24.5 (CH_3), 21.5 (CH_3). Mp: 233 °C (dec). Anal. Calcd for $C_{16}H_{24}Br_2N_2PdS$: C, 35.41; H, 4.46; N, 5.16. Found: C, 35.36; H, 4.72; N, 5.08. MS (ESI): m/z 1005 $[2\ M - Br]^+$.

*cis-Dibromido(1-benzhydryl-3-(2-(isopropylthio)ethyl)-benzimidazolin-2-ylidene-κ^2C,S)palladium(II) (**6**).* The compound was prepared in analogy to **4** from **3** (140 mg, 0.30 mmol, 1.00 equiv), silver(I) oxide (35 mg, 0.15 mmol, 0.50 equiv), and palladium(II) bromide (80 mg, 0.30 mmol, 1.00 equiv). The product was obtained as a yellow solid (197 mg, 0.30 mmol, >99%). ^{1}H NMR (300 MHz, $CDCl_3$, as pyridine adduct): δ 8.98 (d, J_{H-H} = 5 Hz, 2 H, Ar–H), 8.53 (s, 1 H, Ar–H), 7.74 (t, J_{H-H} = 8 Hz, 2 H, Ar–H), 7.47–7.39 (m, 4 H, Ar–H), 7.36–7.27 (m, 7 H, Ar–H, $NCHPh_2$), 7.20 (t, J_{H-H} = 7 Hz, 1 H, Ar–H), 6.96 (t, J_{H-H} = 8 Hz, 1 H, Ar–H), 6.74 (d, J_{H-H} = 8 Hz, 1 H, Ar–H), 5.13–5.00 (m, 2 H, NCH_2), 3.47–3.33 (m, 2 H, SCH_2), 3.21 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, SCH), 1.39 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, as pyridine adduct): δ 165.6 ($C_{carbene}$), 153.1, 138.6, 137.0, 135.5, 129.7, 129.1, 128.8, 125.6, 125.2, 123.6, 123.6, 114.3, 110.9 (Ar–C), 69.0 ($NCHPh_2$), 49.7 (NCH_2), 36.0 (SCH), 29.3 (SCH_2), 24.5 (CH_3). Mp: 173 °C (dec). Anal. Calcd for $C_{25}H_{26}Br_2N_2PdS$: C, 46.00; H, 4.01; N, 4.29. Found: C, 45.89; H, 3.93; N, 4.60. MS (ESI): m/z 572 $[M - Br]^+$.

*cis-Dibromido(1-benzyl-3-(3-(isopropylthio)propyl)-benzimidazolin-2-ylidene-κ^2C,S)palladium(II) (**10**).* The compound was prepared in analogy to **4** from **7** (122 mg, 0.30 mmol, 1.00 equiv),

silver(I) oxide (35 mg, 0.15 mmol, 0.50 equiv), and palladium(II) bromide (80 mg, 0.30 mmol, 1.00 equiv). The product was obtained as a yellow solid (173 mg, 0.29 mmol, 98%). NMR spectra could not be obtained due to the low solubility of the compound in all common deuterated solvents and the fluxionality of its structure. Mp: 170 °C (dec). Anal. Calcd for $C_{20}H_{24}Br_2N_2PdS$: C, 40.67; H, 4.10; N, 4.74. Found: C, 40.21; H, 4.28; N, 4.57. MS (ESI): m/z 511 $[M - Br]^+$.

cis-Dibromido(1-isobutyl-3-(3-(isopropylthio)propyl)-benzimidazolin-2-ylidene-κ²C,S)palladium(II) (**11**). The compound was prepared in analogy to **4** from **8** (111 mg, 0.30 mmol, 1.00 equiv), silver(I) oxide (35 mg, 0.15 mmol, 0.50 equiv), and palladium(II) bromide (80 mg, 0.30 mmol, 1.00 equiv). The product was obtained as a yellow solid (167 mg, 0.30 mmol, >99%). NMR spectra could not be obtained due to the low solubility of the compound in all common deuterated solvents and the fluxionality of its structure. Mp: 218 °C (dec). Anal. Calcd for $C_{17}H_{26}Br_2N_2PdS$: C, 36.68; H, 4.71; N, 5.03. Found: C, 36.27; H, 4.55; N, 5.40. MS (ESI): m/z 1032 $[M - Br]^+$.

cis-Dibromido(1-benzhydryl-3-(2-(isopropylthio)propyl)-benzimidazolin-2-ylidene-κ²C,S)palladium(II) (**12**). The compound was prepared in analogy to **4** from **9** (144 mg, 0.30 mmol, 1.0 equiv), silver(I) oxide (35 mg, 0.15 mmol, 0.50 equiv), and palladium(II) bromide (80 mg, 0.30 mmol, 1.00 equiv). The product was obtained as a yellow solid (200 mg, 0.30 mmol, >99%). NMR spectra could not be obtained due to the low solubility of the compound in all common deuterated solvents and the fluxionality of its structure. Mp: 181 °C. Anal. Calcd for $C_{26}H_{28}Br_2N_2PdS$: C, 46.83; H, 4.23; N, 4.20. Found: C, 46.68; H, 4.30; N, 4.15. MS (ESI): m/z 585 $[M - Br]^+$.

trans-Dibromido(1-benzyl-3-(2-(isopropylthio)ethyl)-benzimidazolin-2-ylidene)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (**13**). Salt **1** (391 mg, 1.00 mmol, 1.00 equiv) and silver(I) oxide (116 mg, 0.50 mmol, 0.50 equiv) were suspended in dichloromethane (15 mL) and stirred at ambient temperature for 15 h shielded from light. $[PdBr_2(^iPr_2\text{-bimy})]_2$ (469 mg, 0.50 mmol, 0.50 equiv) was suspended in dichloromethane (20 mL), and the filtered silver carbene complex solution was added to this suspension. The resulting mixture was stirred for 1 h at ambient temperature. Then it was filtered and concentrated under reduced pressure. The residue was purified by column chromatography (silica, dichloromethane + 5% EtOH). The product was obtained as a yellow solid (644 mg, 0.83 mmol, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68−7.50 (m, 4 H, Ar−H), 7.47−7.28 (m, 5 H, Ar−H), 7.24−7.13 (m, 4 H, Ar−H), 6.23 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, NCH), 6.12 (s, 2 H, NCH_2Ph), 5.99 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, NCH), 5.13−5.02 (m, 2 H, NCH_2), 3.50−3.38 (m, 2 H, SCH_2), 3.13 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, SCH), 1.86 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3), 1.65 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3) 1.37 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 184.5 ($C_{carbene}$), 178.6 ($C_{carbene}$), 136.2, 135.3, 135.2, 134.3, 134.2, 129.5, 128.6, 128.5, 123.8, 123.7, 122.7, 113.4, 113.3, 112.0, 110.9 (Ar−C), 55.4 (NCH), 54.8 (NCH), 54.4 (NCH_2Ph), 49.1 (NCH_2), 36.2 (SCH), 30.5 (SCH_2), 24.4 (CH_3), 21.8 (CH_3) 21.6 (CH_3). Mp: 224 °C (dec). Anal. Calcd for $C_{32}H_{40}Br_2N_4PdS{\cdot}CH_2Cl_2$: C, 45.88; H, 4.90; N, 6.49. Found: C, 46.30; H, 4.58; N, 6.73. MS (ESI): m/z 699 $[M - Br]^+$.

trans-Dibromido(1-isobutyl-3-(2-(isopropylthio)ethyl)-benzimidazolin-2-ylidene)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (**14**). The compound was prepared in analogy to **13** from **2** (391 mg, 1.00 mmol, 1.00 equiv), silver(I) oxide (116 mg, 0.50 mmol, 0.50 equiv), and $[PdBr_2(^iPr_2\text{-bimy})]_2$ (469 mg, 0.50 mmol, 0.50 equiv). The product was obtained as a yellow solid (635 mg, 0.85 mmol, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62−7.56 (m, 2 H, Ar−H), 7.45−7.39 (m, 2 H, Ar−H), 7.31−7.27 (m, 2 H, Ar−H), 7.23−7.19 (m, 2 H, Ar−H), 6.28 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, NCH), 6.24 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, NCH), 5.06−5.01 (m, 2 H, NCH_2), 4.56 (d, $^3J_{H-H}$ = 8 Hz, 2 H, NCH_2), 3.43−3.38 (m, 2 H, SCH_2), 3.18−3.06 (m, 2 H, SCH, CH), 1.85 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3), 1.84 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3), 1.35 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3), 1.13 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 183.9 ($C_{carbene}$), 179.3 ($C_{carbene}$), 136.1, 134.7, 134.3, 134.2, 123.5, 123.5, 122.7, 113.4, 113.3, 111.5, 110.8 (Ar−C), 56.2 (NCH), 54.9 (NCH), 54.6 (NCH_2), 49.0 (NCH_2), 36.2 (SCH), 30.5 (SCH_2), 30.4 (CH), 24.4 (CH_3), 21.7 (CH_3), 21.8 (CH_3) 21.4 (CH_3). Mp: 235 °C (dec). Anal. Calcd for $C_{29}H_{42}Br_2N_4PdS$: C, 46.76; H, 5.68; N, 7.52. Found: C, 46.83; H, 5.59; N, 7.48. MS (ESI): m/z 665 $[M - Br]^+$.

trans-Dibromido(1-benzhydryl-3-(2-(isopropylthio)ethyl)-benzimidazolin-2-ylidene)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (**15**). The compound was prepared in analogy to **13** from **3** (207 mg, 0.44 mmol, 1.00 equiv), silver(I) oxide (51 mg, 0.22 mmol, 0.50 equiv), and $[PdBr_2(^iPr_2\text{-bimy})]_2$ (206 mg, 0.22 mmol, 0.50 equiv). The product was obtained as a yellow solid (229 mg, 0.27 mmol, 61%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.61 (s, 1 H, Ar−H), 7.60−7.57 (m, 1 H, Ar−H), 7.55−7.52 (m, 1 H, Ar−H), 7.44−7.34 (m, 11 H, Ar−H, $NCHPh_2$), 7.22−7.18 (m, 3 H, Ar−H), 6.95 (t, $^3J_{H-H}$ = 8 Hz, 1 H, Ar−H), 6.67 (d, $^3J_{H-H}$ = 8 Hz, 1 H, Ar−H), 6.24 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, NCH), 6.02 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, NCH), 5.13−5.06 (m, 2 H, NCH_2), 3.52−3.46 (m, 2 H, SCH_2), 3.12 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, SCH), 1.85 (d, $^3J_{H-H}$ = 7 Hz, 3 H, CH_3), 1.67 (d, $^3J_{H-H}$ = 7 Hz, 3 H, CH_3), 1.37 (d, $^3J_{H-H}$ = 7 Hz, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 186.3 ($C_{carbene}$), 179.2 ($C_{carbene}$), 138.9, 135.6, 134.8, 134.3, 134.2, 129.6, 129.2, 128.7, 123.4, 122.6, 114.3, 113.4, 113.3, 110.9 (Ar−C), 68.3 (NCH_2Ph), 54.8 (NCH), 54.5 (NCH), 49.1 (NCH_2), 36.3 (SCH), 30.4 (SCH_2), 24.4 (CH_3), 21.7 (CH_3), 21.5 (CH_3). Mp: 136 °C. Anal. Calcd for $C_{38}H_{44}Br_2N_4PdS{\cdot}0.5CH_2Cl_2$: C, 51.52; H, 5.05; N, 6.24. Found: C, 51.75; H, 5.20; N, 6.35. MS (ESI): m/z 775 $[M - Br]^+$.

trans-Dibromido(1-benzyl-3-(2-(isopropylthio)propyl)-benzimidazolin-2-ylidene)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (**16**). The compound was prepared in analogy to **13** from **7** (405 mg, 1.00 mmol, 1.00 equiv), silver(I) oxide (116 mg, 0.50 mmol, 0.50 equiv), and $[PdBr_2(^iPr_2\text{-bimy})]_2$ (469 mg, 0.50 mmol, 0.50 equiv). The product was obtained as a yellow solid (485 mg, 0.61 mmol, 61%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73−7.69 (m, 2 H, Ar−H), 7.66−7.63 (m, 1 H, Ar−H), 7.60−7.56 (m, 2 H, Ar−H), 7.47−7.43 (m, 2 H, Ar−H), 7.40−7.36 (m, 1 H, Ar−H),7.34−7.30 (m, 2 H, Ar−H), 7.28−7.26 (m, 1 H, Ar−H), 7.25−7.20 (m, 2 H, Ar−H), 6.29 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, NCH), 6.22 (s, 2 H, NCH_2Ph), 6.08 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, NCH), 5.10−5.05 (m, 2 H, NCH_2), 3.07 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, SCH), 2.87 (t, $^3J_{H-H}$ = 7 Hz, 2 H, SCH_2), 2.71−2.63 (m, 2 H, CH_2), 1.93 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3), 1.69 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3), 1.39 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 184.1 ($C_{carbene}$), 178.8 ($C_{carbene}$), 136.4, 135.5, 135.2, 134.3, 134.2, 129.4, 128.5, 128.4, 123.6, 123.6, 122.7, 113.3, 111.8, 111.1 (Ar−C), 54.5 (NCH), 54.5 (NCH), 53.2 (NCH_2Ph), 48.0 (NCH_2), 36.0 (SCH), 30.5 (SCH_2), 28.9 (CH_2), 24.1 (CH_3), 21.8 (CH_3), 21.5 (CH_3). Mp: 95 °C. Anal. Calcd for $C_{33}H_{42}Br_2N_4PdS$: C, 49.98; H, 5.34; N, 7.07. Found: C, 50.04; H, 5.39; N, 7.07. MS (ESI): m/z 713 $[M - Br]^+$.

trans-Dibromido(1-isobutyl-3-(2-(isopropylthio)propyl)-benzimidazolin-2-ylidene)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (**17**). The compound was prepared in analogy to **13** from **8** (371 mg, 1.00 mmol, 1.00 equiv), silver(I) oxide (116 mg, 0.50 mmol, 0.50 equiv), and $[PdBr_2(^iPr_2\text{-bimy})]_2$ (469 mg, 0.50 mmol, 0.50 equiv). The product was obtained as a yellow solid (541 mg, 0.71 mmol, 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63−7.60 (m, 2 H, Ar−H), 7.54−7.51 (m, 1 H, Ar−H), 7.45−7.41 (m, 1 H, Ar−H), 7.31−7.28 (m, 2 H, Ar−H), 7.26−7.23 (m, 2 H, Ar−H), 6.35 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, NCH), 6.27 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, NCH), 4.99 (t, $^3J_{H-H}$ = 7 Hz, 2 H, NCH_2), 4.60 (d, $^3J_{H-H}$ = 7 Hz, 2 H, NCH_2), 3.16 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, SCH), 3.01 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, CH), 2.80 (t, $^3J_{H-H}$ = 7 Hz, 2 H, SCH_2), 2.62 (quint, $^3J_{H-H}$ = 7 Hz, 2 H, CH_2), 1.88 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3), 1.86 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3), 1.34 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3), 1.16 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 183.5 ($C_{carbene}$), 179.6 ($C_{carbene}$), 136.1, 135.1, 134.3, 134.2, 123.4, 123.4, 122.7, 113.4, 113.3, 111.4, 111.1 (Ar−C), 56.2 (NCH_2), 54.6 (NCH), 48.0 (NCH_2), 36.1 (SCH), 30.5 (SCH_2), 30.5 (CH), 28.9 (CH_2), 24.2 (CH_3), 21.8 (CH_3), 21.6 (CH_3) 21.5 (CH_3). Mp: 229 °C (dec). Anal. Calcd for $C_{30}H_{44}Br_2N_4PdS$: C, 47.47; H, 5.84; N, 7.38. Found: C, 47.97; H, 6.15; N, 7.63. MS (ESI): m/z 679 $[M - Br]^+$.

trans-Dibromido(1-benzhydryl-3-(2-(isopropylthio)propyl)-benzimidazolin-2-ylidene)(1,3-diisopropyl-benzimidazolin-2-ylidene)palladium(II) (**18**). The compound was prepared in analogy to

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13 from **9** (482 mg, 1.00 mmol, 1.00 equiv), silver(I) oxide (116 mg, 0.50 mmol, 0.50 equiv), and $[PdBr_2(^iPr_2\text{-bimy})]_2$ (469 mg, 0.50 mmol, 0.50 equiv). The product was obtained as a yellow solid (649 mg, 0.76 mmol, 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66 (s, 1 H, Ar−H), 7.58−7.55 (m, 1 H, Ar−H), 7.54−7.48 (m, 2 H, Ar−H), 7.43−7.33 (m, 10 H, Ar−H, $NCHPh_2$), 7.21−7.16 (m, 3 H, Ar−H), 6.93 (t, J_{H-H} = 8 Hz, 1 H, Ar−H), 6.66 (d, J_{H-H} = 8 Hz, 1 H, Ar−H), 6.23 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, NCH), 6.01 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, NCH), 5.04−4.99 (m, 2 H, NCH_2), 3.02 (sept, $^3J_{H-H}$ = 7 Hz, 1 H, SCH), 2.82 (t, $^3J_{H-H}$ = 7 Hz, 2 H, SCH_2), 2.68−2.60 (m, 2 H, CH_2), 1.84 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3), 1.64 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3), 1.33 (d, $^3J_{H-H}$ = 7 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 185.9 ($C_{carbene}$), 179.3 ($C_{carbene}$), 138.9, 135.8, 134.9, 134.2, 134.1, 129.6 129.1, 128.6, 123.3, 122.6, 114.2, 113.3, 113.3, 111.1 (Ar−C), 68.1 ($NCHPh_2$), 54.6 (NCH), 54.5 (NCH), 48.1 (NCH_2), 36.0 (SCH), 30.4 (SCH_2), 28.9 (CH_2), 24.2 (CH_3), 21.8 (CH_3), 21.5 (CH_3). Mp: 131 °C. Anal. Calcd for $C_{39}H_{46}Br_2N_4PdS$: C, 53.90; H, 5.33; N, 6.45. Found: C, 53.64; H, 5.25; N, 6.23. MS (ESI): m/z 789 $[M - Br]^+$.

General Procedure for Catalytic Hydroaminations. A Schlenk tube was charged with precatalyst (10 μmol, 1.0 mol %) under an atmosphere of dry nitrogen. Anhydrous toluene (3 mL) and triflic acid (2.0 μL, 20 μmol, 2.0 mol %) were added, and the resulting suspension was stirred for 5 min at ambient temperature. Then phenylacetylene (219 μL, 2.00 mmol, 2.00 equiv) and 2,6-dimethylaniline (123 μL, 1.00 mmol, 1.00 equiv) were added, and the Schlenk tube was immersed in an oil bath preheated to 100 °C. The mixture was allowed to react for 15 h. After this time, the Schlenk tube was taken out of the oil bath, the suspension was diluted with diethyl ether (10 mL), and decane as an internal standard was added. Samples were analyzed by GC-MS.

General Procedure for the Direct Arylation of 1-Methylpyrrole. A Schlenk tube was charged with precatalyst (10 μmol, 1.0 mol %), 4-bromoacetophenone (199 mg, 1.00 mmol, 1.00 equiv), and potassium acetate (196 mg, 2.00 mmol, 2.00 equiv) under an atmosphere of dry nitrogen. Degassed dimethyl acetamide (3 mL) was added, followed by 1-methylpyrrole (354 μL, 4.00 mmol, 4.00 equiv). The tube was immersed in an oil bath preheated to 150 °C, and the mixture was allowed to react for 20 h. After this time, the Schlenk tube was taken out of the oil bath, the suspension was diluted with diethyl ether (10 mL), and decane as an internal standard was added. Samples were analyzed by GC-MS.

X-ray Diffraction Studies. X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation at 100(2) K, with the SMART suite of programs.[26] Data were processed and corrected for Lorentz and polarization effects with SAINT[27] and for absorption effects with SADABS.[28] Structural solution and refinement were carried out with the SHELXTL suite of programs.[29] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All hydrogen atoms were put at calculated positions. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. A summary of crystallographic data is given in Tables 1−3 and the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures of ^{1}H and ^{13}C NMR spectra for all complexes, CIF files for **4**−**6**, **12**−**16**, and **18**, and tables giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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