ORGANOMETALLICS
Article

Organometallics **2010,** *29,* 1479–1486 1479
DOI: 10.1021/om9010966

Syntheses, Structures, and Catalytic Activities of Hemilabile Thioether-Functionalized NHC Complexes

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Received December 21, 2009

Four imidazolium (**5a**/**b**) and benzimidazolium (**6a**/**b**) salts with hemilabile alkyl-aryl thioether functions have been prepared via a straightforward and modular pathway in order to compare their reactivities toward palladation. Reaction of **5a**/**b** with $Pd(OAc)_2$ gave complex product mixtures, whereas **6a**/**b** afforded the desired bis(benzimidazolin-2-ylidene) complexes **8a**/**b** in good yields. The difference in reactivities of benzimidazole versus imidazole derivatives was attributed to the presence of additional acidic protons at C4/5 positions of the imidazolium ring, leading to competing and unselective deprotonation reactions. The milder Ag-NHC transfer reaction, on the other hand, provided either mono- or bis(imidazolin-2-ylidene) complexes (**9** or **7a**/**b**) in good yields depending on the ligand:metal ratio. The interesting hemilability in monocarbene complex **9** was investigated by spectroscopy and thioether displacement reaction with PPh_3, yielding the mixed NHC-PPh_3 complex **10** in high yields. An initial comparative catalytic study also reveals that the mixed-donor complex **10** exhibits the highest activity among the complexes tested.

Introduction

Donor-functionalization of N-heterocyclic carbenes (NHCs)[1] has become an important theme in organometallic chemistry, attracting considerable attention in recent years. Accordingly, various potentially hemilabile and ditopic NHCs, pincer-type NHCs, and their complexes have been explored and recently reviewed.[2] Notably, N-functionalization with N-, O-, and P-donor groups is relatively common, whereas carbene ligands bearing softer sulfur donors remain surprisingly rare, possibly due to lack of suitable synthetic methodologies, although some thiolato-NHCs,[3−6] thioether-NHCs,[7−9] and thiophene-NHCs[10,11] have been reported. As a contribution to this little explored field, we have recently communicated the hemilabile coordination behavior of a methyl-aryl thioether-functionalized imidazolin-2-ylidene ligand.[12] Herein we provide a more detailed account on the modular design and coordination chemistry of alkyl-aryl thioether-functionalized NHCs derived from imidazole and benzimidazole as well as the applications of their Pd^{II} complexes as catalyst precursors for the aqueous and aerobic Suzuki−Miyaura cross-coupling reaction.

Results and Discussion

Thioether-Functionalized Azolium Salts. The S-donor-functionalized imidazolium and benzimidazolium salts **5** and **6** were synthesized in five steps according to Scheme 1. The first step involved S-alkylation of commercially available thiosalicyclic acid with alkyl bromide to form the 2-alkylmercaptobenzoic acids **1**. The mercaptobenzoates **2** were subsequently formed through esterification of **1** in methanol under acidic conditions. $LiAlH_4$ reduction of **2** under anhydrous conditions and subsequent acidification gave rise to the formation of the benzyl alcohols **3**, which then underwent substitution reaction with PBr_3 to furnish the benzyl bromides **4**. N-Alkylation of *N*-methylimidazole and *N*-methylbenzimidazole finally afforded the respective carbene precursors in overall yields of 63% (**5a**), 64% (**5b**), 57% (**6a**), and 59% (**6b**) over five steps.

The formation of the organic compounds in each step can be nicely traced by ^1H NMR spectroscopy. For example a new singlet due to the OCH_3 group is detected upfield at 3.92 (**2a**) or 3.95 ppm (**2b**) on formation of the esters **2**. Upon reduction to the alcohols **3**, a more downfield singlet attributed to the benzylic CH_2 protons can be observed at 4.70 (**3a**)

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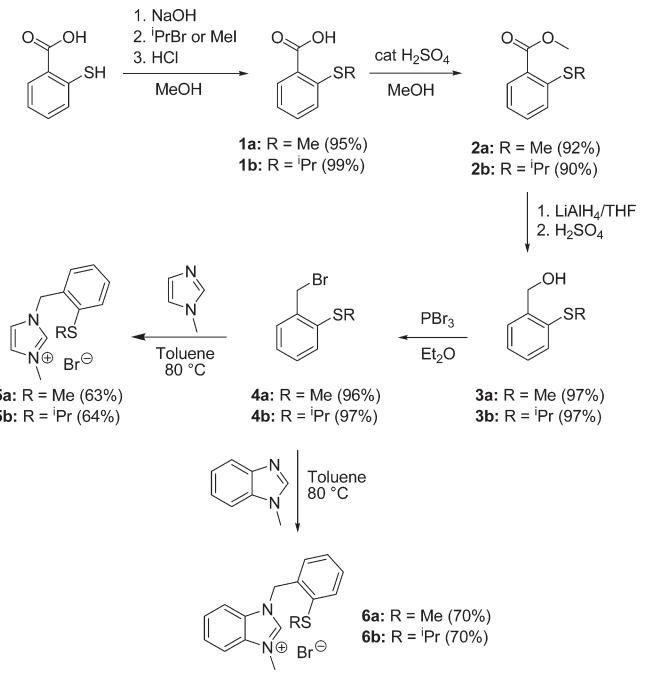
Published on Web 02/18/2010

Scheme 1. Synthetic Pathway for Thioether-Functionalized Azolium Salts



or 4.79 ppm (**3b**) instead. In addition, a broad signal due to the OH proton was observed at 2.60 (**3a**) or 2.27 ppm (**3b**). This broad signal disappears when compounds **3** undergo substitution reaction to form benzyl bromides **4**. The formation of the imidazolium and benzimidazolium salts **5** and **6** was finally corroborated by characteristic downfield signals at 10.37 (**5a**), 10.26, (**5b**), 11.25 (**6a**), and 11.34 ppm (**6b**) for the NCHN protons. The identity of these carbene precursors **5** and **6** was further confirmed by their ESI mass spectra, which in all cases show base peaks for the $[M - Br]^+$ fragments. While the benzimidazolium salts **6** are both solids, the properties of their imidazolium analogues are more prone to influences from the S-alkyl group. The use of the more aliphatic S-isopropyl group results in a room-temperature ionic liquid, whereas an S-methyl substituent gives rise to a hygroscopic solid.

Palladium(II) Bis(Carbene) Complexes. The standard reaction of $Pd(OAc)_2$ with 2 equiv of azolium salt was initially chosen in an attempt to prepare bis(carbene) Pd^{II} complexes and to study the coordination behavior of thioether-functionalized NHC ligands. However, heating a mixture of **5a** and $Pd(OAc)_2$ in acetonitrile at 90 °C gave rise to a complex product mixture from which only *cis*-**7a** could be isolated in a low yield of 38%. The difficulty of carbene formation and subsequent coordination to Pd^{II} under the relatively harsh reaction conditions can be attributed to competing processes such as (i) nonselective coordination of the soft sulfur atom, (ii) competing deprotonation at C4/C5-positions, or (iii) competing deprotonation of the benzylic protons. Thus the alternative and milder Ag-carbene transfer method was explored instead.[13] Indeed, an isomeric mixture of bis(carbene) complexes *cis*-**7a**, *trans-anti*-**7a**, and *trans-syn*-**7a** was obtained in 98% overall yield when $[PdBr_2(CH_3CN)_2]$ was treated with Ag-carbene species generated *in situ* by mixing Ag_2O and 2 equiv of **5a** in CH_2Cl_2 (Scheme 2).

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The formation of these bis(carbene) complexes is indicated by a base peak in the ESI mass spectrum at $m/z = 623$ for the $[M - Br]^+$ complex fragment. Due to different solubilities, *cis*- and *trans*-isomers can be separated by washing with acetone. The remaining insoluble yellow powder (53%) contains an approximately 1:1 rotameric mixture of *trans*-**7a**, which cannot be further separated probably due to the low rotational barrier. ^1H and ^{13}C NMR spectra in $CDCl_3$ of the latter show two sets of signals with $C_{carbene}$ resonances at 169.9 and 169.8 ppm, corresponding to the *syn*- and *anti*-rotamers, respectively. Removal of the solvent from the acetone filtrate and subsequent recrystallization from $CHCl_3$ yielded an off-white powder of *cis*-**7a** (~45%). Its ^1H NMR spectrum in CD_3CN is dominated by broad signals indicating a restricted rotation of the $Pd-C_{carbene}$ bonds in the *cis*-isomer. ^{13}C NMR data, on the other hand, could not be obtained due to insufficient solubility. However, an X-ray diffraction analysis on single crystals of the solvate *cis*-**7a**·2DMF, obtained by vapor diffusion of diethyl ether into a concentrated DMF solution, confirms the *cis*-arrangement of the NHC ligands in the essentially square-planar complex with the bulky methylmercaptobenzyl groups *anti* to each other (Figure 1). The two $Pd-C_{carbene}$ bonds of 1.982(3) and 1.992(3) Å and the Pd−Br bonds of 2.4856(4) and 2.4785(3) Å are in the typical range found for *cis*-standing dibromobis(carbene) Pd^{II} complexes.[14]

A similar reaction sequence employing imidazolium salt **5b** also gave an approximately 1:1 mixture of *trans-anti*-**7b** and *trans-syn*-**7b**, as indicated by two sets of signals with similar integrals in the ^1H NMR spectrum and an ESI-MS base peak at $m/z = 679$ for the $[M - Br]^+$ cation. The two rotamers equilibrate in solution, indicating a certain degree of rotational freedom of the $Pd-C_{carbene}$ bonds. Surprisingly, *cis*-isomers were not detected. The *trans*-configuration is confirmed by ^{13}C NMR spectroscopy, which shows the presence of two closely spaced $C_{carbene}$ signals at 169.7 and 169.8 ppm for the two rotamers, respectively. Upon slow evaporation of a concentrated CH_2Cl_2 solution, single crystals of *trans-anti*-**7b** formed as the supposedly more favorable rotamer in the solid state (Figure 2). Compared to the bond parameters in *cis*-**7a** the *trans*-configuration in *trans-anti*-**7b** leads to a significant lengthening of the Pd−C bond to 2.046(6) Å accompanied by a shortening of the Pd−Br bond to 2.4385(8) Å, in line with the different *trans*-influences of the ligands involved. Notably, a remote change seven bonds away from the Pd^{II} center can lead to the preferred formation of *trans*-complexes.

The benzimidazolium salts **6a/b** react differently and more cleanly than their imidazole analogues due to the absence of any acidic protons on the heterocycle. Thus the reaction with $Pd(OAc)_2$ could proceed smoothly in DMSO at 90 °C, giving preferably the *cis*-configured complexes *cis*-**8a/b** in yields of 67% and 89%, respectively. The *cis*-configuration restricts rotation of both *N*-benzyl and Pd−C bonds leading to diastereotopy of the benzylic protons, which in turn resonate as two doublets (6.07 and 5.67 ppm for *cis*-**8a**; 6.14 and 5.78 ppm for *cis*-**8b**) with geminal coupling constants of around $^2J(H,H) = 17.0$ Hz. The observation of only one AA′ spin-system for each complex excludes the presence of *cis*-rotamers,

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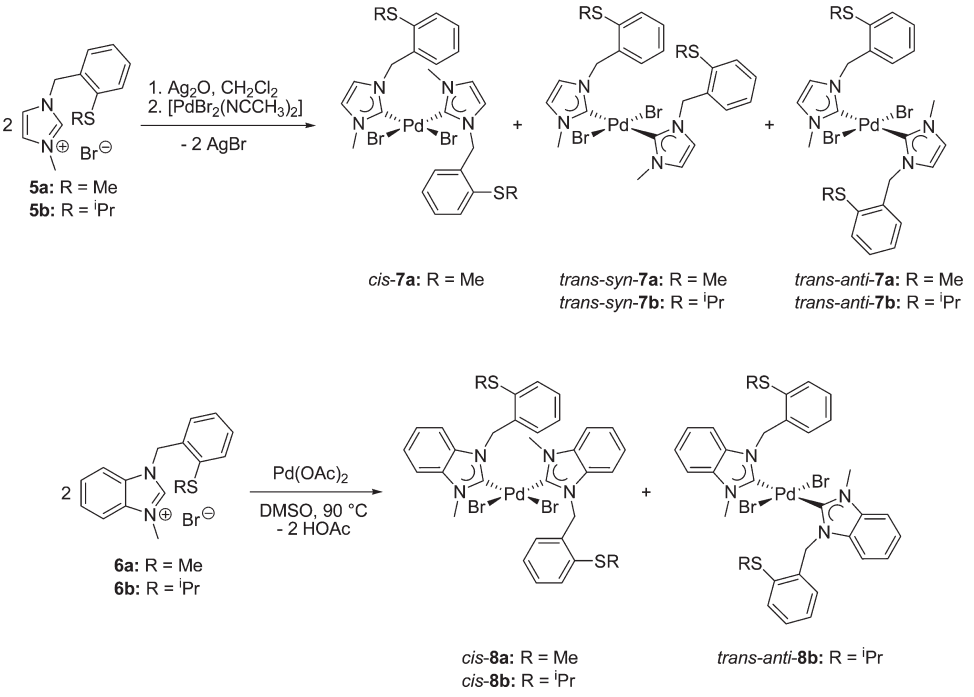
Scheme 2. Synthetic Pathway for Pd^{II}−Bis(carbene) Complexes



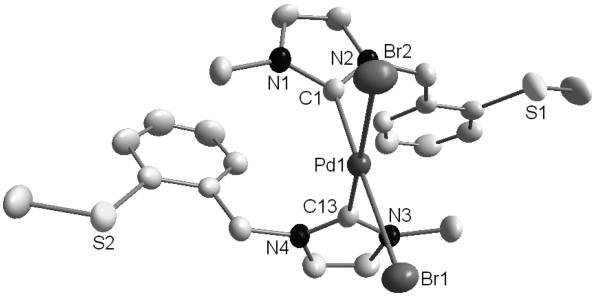


Figure 1. Molecular structure of *cis*-**7a**·2DMF showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1−C1 1.982(3), Pd1−C13 1.992(3), Pd1−Br1 2.4856(4), Pd1−Br2 2.4785(3), C1−N1 1.350(4), C1−N2 1.348(4), C13−N3 1.347(4), C13−N4 1.357(4); C1−Pd1−C13 92.84(13), C1−Pd1−Br2 86.57(9), C13−Pd1−Br1 87.06(9), Br1−Pd1−Br2 93.539(16), N1−C1−N2 104.6(3), N3−C13−N4 104.8(3).

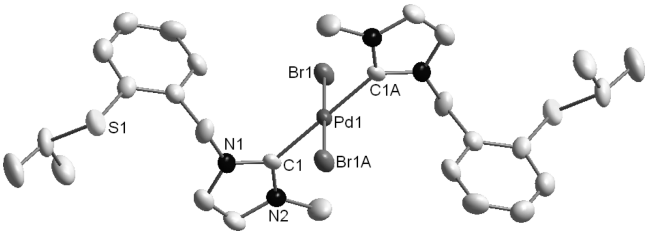


Figure 2. Molecular structure of complex *trans-anti*-**7b** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1−C1 2.046(6), Pd1−Br1 2.4385(8), N1−C1 1.344(8), N2−C1 1.331(8); C1−Pd1−Br1 92.34(17), C1−Pd1−Br1A 87.66(17), Br1−Pd1−Br1A 180.00(4), N1−C1−N2 105.1(6).

which have been observed for thiophene-functionalized derivatives.[15] This is further substantiated by ^{13}C NMR spectra showing only one carbene signal for each *cis*-bis(carbene) complex at 175.1 ppm (*cis*-**8a**) and 174.4 ppm (*cis*-**8b**), respectively. X-ray diffraction studies on single crystals of *cis*-**8a** grown from a concentrated CH_3CN solution confirmed the sterically more favorable *cis-anti*-arrangement of the complex similar to that of *cis*-**7a**. The Pd−C and Pd−Br bonds of 1.977(4) and 2.4652(5) Å are comparable to those found in the thiophene-functionalized analogue (Figure 3).[15]

Attempts to obtain single crystals of *cis*-**8b** on the other hand proved unsuccessful. Instead *cis*−*trans* isomerization occurs upon prolonged standing, affording only a few single crystals, which were analyzed as *trans-anti*-**8b** (Figure 4). As observed for the imidazolin-2-ylidene analogues (*vide supra*), the *trans*-configuration of the two carbene ligands leads to longer Pd−C [2.020(4) Å] and shorter Pd−Br bonds [2.4328(5) Å] compared to those in *cis*-**8a**.

Palladium(II) Monocarbene Complexes. In an initial attempt to enforce thioether coordination through abstraction of the bromo ligands, *trans*-**7b** was treated with 2 equiv of $AgBF_4$. Disappointingly, this reaction gave rise to an intractable dark reaction mixture possibly due to decomposition induced by Ag^I-promoted thioether cleavage.[16] Alternatively, it was anticipated that a monocarbene complex with two stabilizing bromo ligands should also allow thioether coordination. Thus, we have attempted the Ag-carbene transfer reaction in a 1:1 ligand to Pd ratio (Scheme 3).[12]

The ^1H NMR spectrum of the reaction product in $CDCl_3$ shows very broad signals at ambient temperature. Upon cooling to −30 °C, two doublets at 5.00 and 5.85 ppm were resolved for the nonequivalent benzylic protons, which

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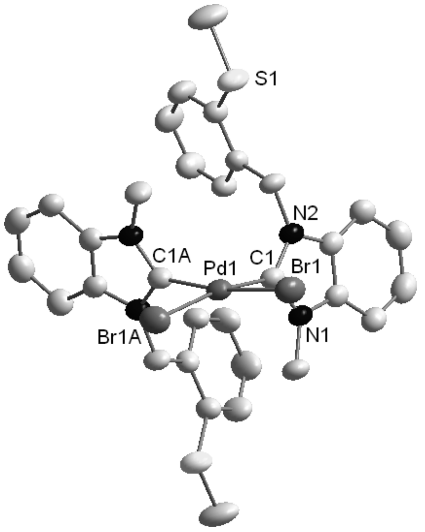

Figure 3. Molecular structure of complex *cis*-**8a** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1−C1 1.977(4), Pd1−Br1 2.4652(5), C1−N1 1.354(4), C1−N2 1.368(5), N1−C2 1.379(5), N1−C8 1.460(5), N2−C7 1.394(5), N2−C9 1.451(4), C2−C7 1.381(5); C1−Pd1−C1A 95.6(2), Br1−Pd1−Br1A 94.07(3), C1−Pd1−Br1 85.96(10), C1A−Pd1−Br1 170.40(10), C1−Pd1−Br1A 170.40(10), C1A−Pd1−Br1A 85.96(10), N1−C1−N2 105.5(3).

indirectly indicates coordination of the sulfur function. In addition, two sets of signals are observed for the $N-CH_3$ and the $S-CH_3$ groups, pointing to a rather complex mixture (*vide infra*). The identity of complex **9** was finally confirmed by X-ray diffraction. The complex adopts a distorted square-planar geometry with the carbene and sulfur donors in *cis*-position, resulting in a seven-membered chelate ring, which is in a boat-like conformation (Figure 5). The coordination of the sulfur atom leads to a significantly small dihedral angle of 65.155(77)° between the carbene ring plane and the $PdCSBr_2$ coordination plane. The longer Pd−Br2 bond [2.4792(4) vs 2.4508(4) Å for Pd−Br1] *trans* to the carbene reflects its strong *trans*-influence.

The complicated ^{1}H NMR spectrum of complex **9** was mainly attributed to two dynamic processes in solution. The first process involves flipping of the seven-membered ring, which slows down upon cooling, giving rise to the inequivalent benzylic protons observed at low temperature. The second process involves reversible de- and recoordination of the sulfur donor in a hemilabile fashion. Decoordination results in a formally unsaturated metal center, which stabilizes itself upon dimerization. The two dynamic processes are in equilibrium with at least five species (Scheme 4). The situation is further complicated due to the fact that the thioether donor becomes chiral upon coordination.

To confirm the hemilabile behavior of the thioether-NHC ligand, one equivalent (based on Pd) of PPh_3 was added to a solution of **9** in CH_3CN. The stronger phosphine donor is expected to cleave potential dimeric complexes as well as the weaker Pd−S(Ar)R bond in **9**. Indeed, the addition of PPh_3 leads to a clean and well-resolved ^{1}H NMR spectrum corroborating the formation of the mixed NHC-phosphine complex **10** as the sole product. Two doublets are observed at 5.76 and 4.71 ppm, respectively, for the diastereotopic benzylic protons with a geminal coupling constant of

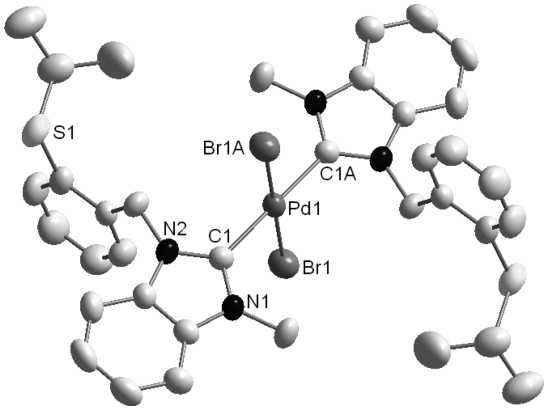

Figure 4. Molecular structure of complex *trans-anti*-**8b**·CH_2Cl_2 showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1−C1 2.020(4), Pd1−Br1 2.4328(5), N1−C1 1.355(5), N1−C2 1.391(4); C1−Pd1−C1A 180.0(3), Br1−Pd1−Br1A 180.0, C1−Pd1−Br1 89.98(11), C1A−Pd1−Br1 90.02(11), N2)−C1−N1 105.9(3).

^2J(H,H) = 14.3 Hz. This observation is in line with a hindered rotation of the Pd−$C_{carbene}$ bond due to the steric bulk of the phosphine ligand and indirectly confirms the *cis* arrangement of the NHC and PPh_3 ligands. The ^{13}C NMR signal for the carbenoid carbon appears at 162.7 ppm as a singlet, and coupling to the *cis*-standing ^{31}P nucleus could not be resolved under the given conditions. However, the presence of the phosphine donor is evidenced by a resonance at 27.13 ppm in the ^{31}P NMR spectrum. Single crystals obtained from a saturated CD_3CN solution were subjected to an X-ray diffraction analysis, and the molecular structure of **10** is shown in Figure 6. The metal center is coordinated by one NHC, one phosphine, and two bromo ligands in a distorted square-planar fashion. The former two are found in a *cis* arrangement, which is thermodynamically favored due to the transphobia effect of phosphines.[17] Furthermore, it can be clearly seen that the steric bulk of the phosphine ligand prevents a free rotation of the Pd−$C_{carbene}$ bond.

Suzuki−Miyaura Catalysis. In order to compare the catalytic performance of bis- versus monocarbene complexes, we tested five selected complexes with S-Me donor groups for their catalytic activities in the Suzuki−Miyaura coupling of aryl bromides and chlorides in/on pure water under aerobic conditions. The results summarized in Table 1 show that all complexes are highly active in the coupling of activated 4-bromobenzaldehyde, giving quantitative yields already at ambient temperature (entries 1−5). Furthermore, the coupling of 4-bromoacetophenone reveals that among bis(carbene) species *cis*-**7a** and *cis*-**8a** perform slightly better than the *trans*-analogue *trans*-**7a** (entries 6, 8 vs 7). The superiority of *cis*- versus *trans*-complexes has also been observed for the Mizoroki−Heck reaction.[18]

The best performance, however, was exhibited by the mixed NHC-phosphine complex **10**. The coupling of deactivated 4-bromoanisole generally gave very low yields of $<30\%$. However, it can be quantitatively coupled by all complexes at elevated

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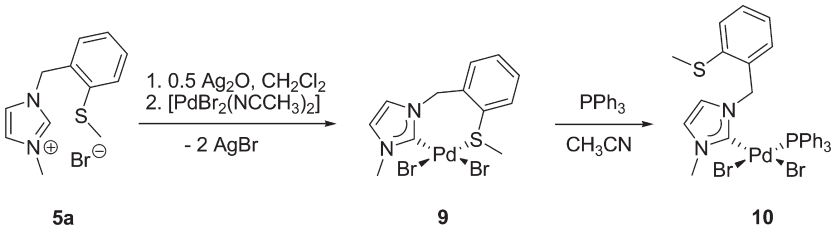
Scheme 3. Synthetic Pathway for Pd^{II}−Monocarbene Complexes



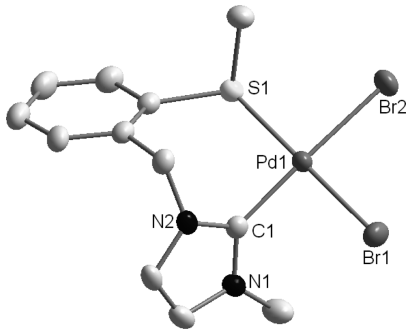


Figure 5. Molecular structure of **9** showing 50% probability ellipsoids. Selected bond lengths [Å] and angles [deg]: Pd1−C1 1.971(3), Pd1−S1 2.3079(3), Pd1−Br1 2.4508(4), Pd1−Br2 2.4792(4), C1−N1 1.343(4), C1−N2 1.335(4); C1−Pd1−S1 93.65(9), C1−Pd1−Br1 86.53(8), S1−Pd1−Br2 86.94(2), Br1−Pd1−Br2 93.070(13), N1−C1−N2 105.8(3).

temperatures and with the addition of $[N(n\text{-}C_4H_9)_4]Br$ (entries 11−15).[19] It is believed that such ammonium salts help to stabilize reactive intermediates through formation of ion-pairs and hampering their aggregation.[18] Disappointingly, the coupling of more challenging aryl chlorides under the same conditions gave rather poor results for most complexes with the exception of mixed NHC-phosphine complex **10**. It is noteworthy that **10** gave the best yields of 52% and 44%, respectively (entries 20 and 25), which is superior to previously reported Pd^{II}-monocarbene complexes under similar conditions.[19]

Conclusion

We have presented a straightforward and modular synthetic pathway to thioether-functionalized N-heterocyclic carbene ligands derived from imidazole and benzimidazole. Their coordination chemistry with respect to the formation of mono- versus bis(carbene) complexes have been studied in detail, revealing their hemilabile nature. Moreover, an initial catalytic investigation demonstrated that the mixed NHC-phosphine complex **10** showed overall the best performance. Research in our laboratory is currently underway to extend the coordination chemistry of these hemilabile ligands to other late transition metals and to study their potential applications in catalysis.

Experimental Section

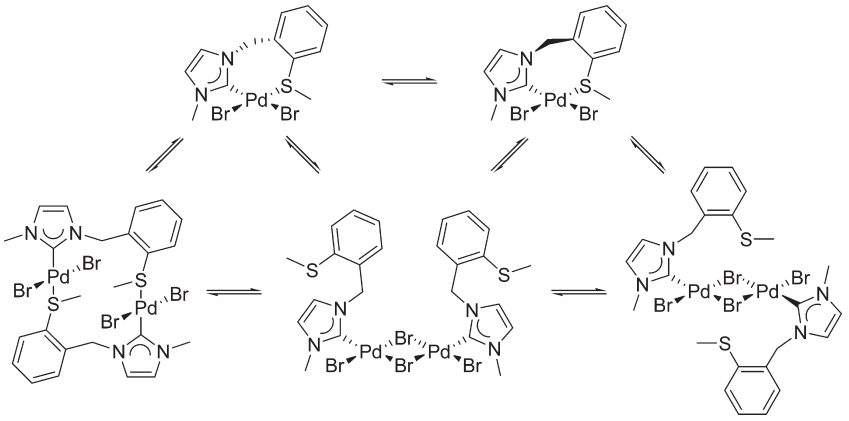
General Considerations. Unless otherwise noted all operations were performed without taking precautions to exclude air and moisture. All solvents and chemicals were used as received without any further treatment if not noted otherwise. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker ACF 300 spectrometer, and the chemical shifts (δ) were internally referenced to the residual solvent signals relative to tetramethylsilane (^1H, ^{13}C) or externally to 85% H_3PO_4 (^{31}P). Mass spectra were measured using a Finnigan MAT LCQ (ESI) spectrometer. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

2-Methylmercaptobenzoic Acid (1a) and 2-Isopropylmercaptobenzoic Acid (1b). Aqueous NaOH (10 mL of a 25% solution, 62.5 mmol) was added to a solution of thiosalicyclic acid (3.084 g, 20.0 mmol) in methanol (55 mL). The reaction mixture was stirred for 20 min at room temperature, and methyl iodide (2.75 mL, 44.0 mmol for **1a**) or isopropyl bromide (4.20 mL, 44.9 mmol for **1b**) was added. The reaction mixture was heated under reflux overnight at 70 °C. The reaction mixture was allowed to cool to room temperature, and the solvent was removed *in vacuo*. The residue was dissolved in deionized water (50 mL) and acidified with concentrated HCl (37%). The mixture was extracted with diethyl ether (1 × 50 mL, 3 × 30 mL), and the combined organic layers were dried over $MgSO_4$ and filtered. Removal of the solvent *in vacuo* yielded the product as an off-white powder. **1a**, 3.196 g (19.00 mmol), 95% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 8.15 (dd, $^3J(H,H)$ = 7.9 Hz, $^4J(H,H)$ = 1.5 Hz, 1 H, Ar−H), 7.53 (td, $^3J(H,H)$ = 7.7 Hz, $^4J(H,H)$ = 1.6 Hz, 1 H, Ar−H), 7.30 (d, $^3J(H,H)$ = 8.1 Hz, 1 H, Ar−H), 7.20 (td, $^3J(H,H)$ = 7.6 Hz, $^4J(H,H)$ = 1.1 Hz, 1 H, Ar−H), 2.48 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 171.4 (COOH), 144.4, 133.3, 132.5, 125.5, 124.4, 123.5 (Ar−C), 15.6 (CH_3). **1b**, 3.870 g (19.72 mmol), 99% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 8.15 (dd, $^3J(H,H)$ = 7.8 Hz, $^4J(H,H)$ = 1.1 Hz, 1 H, Ar−H), 7.52−7.43 (m, 2 H, Ar−H), 7.28−7.23 (m, 1 H, Ar−H), 3.51 (sep, $^3J(H,H)$ = 6.6 Hz, 1 H, CH), 1.39 (d, $^3J(H,H)$ = 6.6 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 171.2 (COOH), 140.6, 133.6, 133.3, 129.9, 129.1, 125.9 (Ar−C), 37.4 (CH), 23.3 (CH_3).

Methyl 2-Methylmercaptobenzoate (2a) and Methyl 2-Isopropylmercaptobenzoate (2b). Concentrated H_2SO_4 (1 mL) was added to a solution of **1a** (3.1 g, 18.43 mmol) or **1b** (3.8 g, 19.36 mmol) in methanol (30 mL). The reaction mixture was heated under reflux at 70 °C for 3 h and allowed to cool to ambient temperature. Deionized water (50 mL) was added, and the mixture was extracted with diethyl ether (1 × 50 mL, 3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and filtered. Removal of the solvent *in vacuo* yielded the product as an off-white powder (**2a**) or yellow liquid (**2b**). **2a**, 3.090 g (16.96 mmol), 92% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 8.00 (dd, $^3J(H,H)$ = 7.9 Hz, $^4J(H,H)$ = 1.5 Hz, 1 H, Ar−H), 7.48 (td, $^3J(H,H)$ = 7.7 Hz, $^4J(H,H)$ = 1.6 Hz, 1 H, Ar−H), 7.28 (d, $^3J(H,H)$ = 7.7 Hz, 1 H, Ar−H), 7.16 (td, $^3J(H,H)$ = 7.6 Hz, $^4J(H,H)$ = 1.2 Hz, 1 H, Ar−H), 3.92 (s, 3 H, OCH_3), 2.46 (s, 3 H, SCH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 166.8 (COOH), 143.2, 132.4, 131.2, 126.7, 124.3, 123.3 (Ar−C), 51.9 (OCH_3), 15.5 (SCH_3). **2b**, 3.663 g (17.42 mmol), 90% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 7.92 (dd, $^3J(H,H)$ = 7.7 Hz, d, $^4J(H,H)$ = 1.5 Hz, 1 H, Ar−H), 7.43−7.29 (m, 2 H, Ar−H), 7.20 (td, $^3J(H,H)$ = 7.2 Hz, d, $^4J(H,H)$ = 2.0 Hz, 1 H, Ar−H), 3.95 (s, 3 H, OCH_3), 3.56 (sep, $^3J(H,H)$ = 6.8 Hz, 1 H, CH), 1.41 (d, $^3J(H,H)$ = 6.6 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 167.1

(19) (a) Huynh, H. V.; Han, Y.; Ho, J. H. H.; Tan, G. K. *Organometallics* **2006**, *25*, 3267. (b) Han, Y.; Hong, Y.-T.; Huynh, H. V. *J. Organomet. Chem.* **2008**, *693*, 3159.

Scheme 4. Dynamic Processes Due to the Hemilabile Ligand in Complex 9



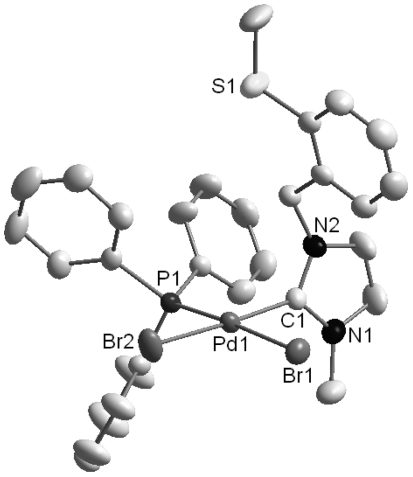


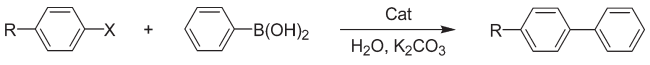
Figure 6. Molecular structure of **10** showing 50% probability ellipsoids. Selected bond lengths [Å] and angles [deg]: Pd1−C1 1.986(3), Pd1−P1 2.2642(8), Pd1−Br1 2.4775(4), Pd1−Br2 2.4785(3), C1−N1 1.349(4), C1−N2 1.350(4); C1−Pd1−P1 92.18(9), C1−Pd1−Br1 86.41(9), P1−Pd1−Br2 91.03(2), Br1−Pd1−Br2 90.763(15), N1−C1−N2 105.1(3).

(COOH), 140.3, 131.8, 130.9, 129.3, 127.6, 124.1 (Ar−C), 52.0 (OCH_3), 35.4 (CH), 22.6 (CH_3).

2-Methylmercaptobenzyl Alcohol (3a) and 2-Isopropylmercaptobenzyl Alcohol (3b). 2a (3 g, 16.46 mmol) or **2b** (3 g, 17.12 mmol) was dissolved in anhydrous THF (20 mL) and added dropwise to a suspension of $LiAlH_4$ (1.2 g, 31.62 mmol) in anhydrous THF (30 mL). The reaction mixture was heated under reflux overnight at 75 °C. Deionized water was then added dropwise to hydrolyze excess $LiAlH_4$, and the resulting suspension was acidified with sulfuric acid. The mixture was extracted with diethyl ether (1 × 50 mL, 3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and filtered. Removal of the solvent *in vacuo* yielded the product as a yellow liquid. **3a**, 2.462 g (15.97 mmol), 97% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36−7.12 (m, 4 H, Ar−H), 4.70 (s, 2 H, CH_2), 2.60 (brs, 1 H, OH), 2.44 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 138.9, 136.4, 128.1, 127.6, 126.2, 125.3 (Ar−C), 62.8 (CH_2), 25.5 (SCH_3). **3b**, 3.027 g (16.61 mmol), 97% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46−7.24 (m, 4 H, Ar−H), 4.79 (s, 2 H, CH_2), 3.39 (sep, ^3J(H,H) = 6.6 Hz, 1 H, CH), 2.27 (brs, 1 H, OH), 1.30 (d, ^3J(H,H) = 6.6 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 142.5, 134.0, 133.1, 128.7, 128.3, 127.6 (Ar−C), 64.2 (CH_2), 39.1 (CH), 23.5 (CH_3).

2-Methylmercaptobenzyl Bromide (4a) and 2-Isopropylmercaptobenzyl Bromide (4b). PBr_3 (0.84 mL, 9.00 mmol) was added dropwise to a solution of **3a** (2.4 g, 15.56 mmol) or **3b** (3 g, 16.46 mmol) in diethyl ether (10 mL) at 0 °C. The solution was stirred for 1 h at ambient temperature, and methanol (1.5 mL) was then added. The mixture was diluted with deionized water (50 mL), and the mixture was extracted with diethyl ether (1 × 50 mL, 3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and filtered. Removal of the solvent *in vacuo* yielded the product as a yellow liquid. **4a**, 3.243 g (14.94 mmol), 96% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34−7.09 (m, 4 H, Ar−H), 4.63 (s, 2 H, CH_2), 2.49 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 139.0, 136.0, 130.8, 129.7, 127.3, 125.8 (Ar−C), 32.4 (CH_2), 16.5 (CH_3). **4b**, 3.915 g (15.97 mmol), 97% yield. ^{1}H NMR (300 MHz,

Table 1. Suzuki−Miyaura Cross-Coupling Reactions[a] in/on Water



X = Br, Cl
R = $COCH_3$, CHO, OCH_3

entry	catalyst	aryl halide	*t* [h]	temp [°C]	yield [%][b]
1	*cis*-**7a**	4-bromobenzaldehyde	8	RT	> 99
2	*trans*-**7a**	4-bromobenzaldehyde	8	RT	> 99
3	*cis*-**8a**	4-bromobenzaldehyde	8	RT	> 99
4	**9**	4-bromobenzaldehyde	8	RT	> 99
5	**10**	4-bromobenzaldehyde	8	RT	> 99
6	*cis*-**7a**	4-bromoacetophenone	8	RT	98
7	*trans*-**7a**	4-bromoacetophenone	8	RT	84
8	*cis*-**8a**	4-bromoacetophenone	8	RT	90
9	**9**	4-bromoacetophenone	8	RT	85
10	**10**	4-bromoacetophenone	8	RT	> 99
11[c]	*cis*-**7a**	4-bromoanisole	21	85	> 99
12[c]	*trans*-**7a**	4-bromoanisole	21	85	> 99
13[c]	*cis*-**8a**	4-bromoanisole	21	85	> 99
14[c]	**9**	4-bromoanisole	21	85	> 99
15[c]	**10**	4-bromoanisole	21	85	> 99
16[c]	*cis*-**7a**	4-chlorobenzaldehyde	21	85	7
17[c]	*trans*-**7a**	4-chlorobenzaldehyde	21	85	11
18[c]	*cis*-**8a**	4-chlorobenzaldehyde	21	85	3
19[c]	**9**	4-chlorobenzaldehyde	21	85	8
20[c]	**10**	4-chlorobenzaldehyde	21	85	52
21[c]	*cis*-**7a**	4-chloroacetophenone	21	85	3
22[c]	*trans*-**7a**	4-chloroacetophenone	21	85	9
23[c]	*cis*-**8a**	4-chloroacetophenone	21	85	23
24[c]	**9**	4-chloroacetophenone	21	85	25
25[c]	**10**	4-chloroacetophenone	21	85	44

[a] Reaction conditions: 1 mmol of aryl halide; 1.5 mmol of phenylboronic acid; 3 mL of water; 2 equiv of K_2CO_3; 1 mol % of catalyst. [b] Yields were determined by ^{1}H NMR spectroscopy for an average of two runs. [c] With addition of 1.5 equiv of $[N(n\text{-}C_4H_9)_4]Br$.

$CDCl_3$): δ 7.48−7.18 (m, 4 H, Ar−H), 4.74 (s, 2 H, CH_2), 3.46 (sep, ^3J(H,H) = 6.6 Hz, 1 H, CH), 1.32 (d, ^3J(H,H) = 6.6 Hz, 6 H, CH_3).

Imidazolium Salts 5a and 5b. 4a or **4b** (10 mmol) was added to a solution of 1-methylimidazole (0.80 mL, 10 mmol) in toluene. The reaction mixture was stirred overnight at 80 °C. An immiscible layer was formed and the toluene was decanted. The remaining yellow oil was washed with toluene and diethyl ether and subsequently dried *in vacuo*. **5a** solidifies in the refrigerator overnight, giving a white hygroscopic solid, whereas **5b** was obtained as viscous yellow oil. **5a**, 2.878 g (9.62 mmol), 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.37 (s, 1 H, NCHN), 7.65 (dd, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.2 Hz, 1 H, Ar−H), 7.43−7.22 (m, 5 H, Ar−H + CH_{Imd}), 5.64 (s, 2 H, CH_2), 4.10 (s, 3 H, NCH_3), 2.50 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 138.4 (NCN), 137.4, 131.2, 130.7, 130.5, 127.0, 126.2 (Ar−C), 123.4, 121.8 (CH_{Imd}), 51.1 (CH_2), 36.8 (NCH_3), 16.1 (SCH_3). MS (ESI, positive ions) *m*/*z* (%): 219 (100) [M − Br]$^+$. **5b**, 3.118 g (9.53 mmol), 76% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.26 (s, 1 H, NCHN), 7.72 (dd, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.7 Hz, 1 H, Ar−H), 7.55−7.16 (m, 5 H, Ar−H + CH_{Imd}), 5.72 (s, 2 H, CH_2), 4.10 (s, 3 H, NCH_3), 3.40 (sep, ^3J(H,H) = 6.6 Hz, 1 H, CH), 1.29 (d, ^3J(H,H) = 6.7 Hz, 6 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 137.2 (NCN), 135.6, 134.1, 133.0, 131.3, 130.1, 128.1 (Ar−C), 123.4, 121.7 (CH_{Imd}), 51.3 (CH_2), 39.4 (NCH_3), 36.8 (CH), 22.9 (CH_3). MS (ESI, positive ions) *m*/*z* (%): 247 (100) [M − Br]$^+$.

Benzimidazolium Salt 6a. 4a (0.637 g, 2.93 mmol) was added to a solution of 1-methylbenzimidazole (0.338 g, 2.56 mmol) in toluene (5 mL). The reaction mixture was stirred overnight at 90 °C. The white precipitate formed was filtered and washed with toluene and diethyl ether. The product was dried *in vacuo*, giving a white powder. **6a**, 0.623 g (1.78 mmol), 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.25 (s, 1 H, NCHN), 7.69−7.51 (m, 5 H, Ar−H), 7.40−7.31 (m, 2 H, Ar−H), 7.25−7.20 (m, 1 H, Ar−H), 5.88 (s, 2 H, CH_2), 4.31 (s, 3 H, NCH_3), 2.51 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 144.4 (NCHN), 138.6, 132.7, 131.8, 131.0, 130.9, 130.8, 128.1, 127.8, 127.8, 127.0, 114.4, 113.4 (Ar−C), 50.0 (CH_2), 34.6 (NCH_3), 17.2 (SCH_3). MS (ESI): *m*/*z* = 269 [M − Br]$^+$.

Benzimidazolium Salt 6b. 4b (0.544 g, 2.22 mmol) was added to a solution of 1-methylbenzimidazole (0.268 g, 2.03 mmol) in toluene (5 mL). The reaction mixture was stirred overnight at 90 °C. The volatiles were removed *in vacuo*, and the viscous brown mixture obtained was washed with copious amounts of diethyl ether. Upon standing in diethyl ether, a white precipitate formed. The diethyl ether was decanted, and the product was dried *in vacuo* to obtain a white powder. **6b**, 0.536 g (1.42 mmol), 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.34 (s, 1 H, NCHN), 7.69−7.49 (m, 6 H, Ar−H), 7.35−7.27 (m, 2 H, Ar−H), 6.01 (s, 2 H, CH_2), 4.30 (s, 3 H, NCH_3), 3.36 (sep, ^3J(H,H) = 6.7 Hz, 1 H, SCH), 1.28 (d, ^3J(H,H) = 6.7 Hz, 6 H, SCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 144.3 (NCHN), 135.6, 134.8, 134.6, 132.7, 131.7, 130.9, 130.5, 129.1, 127.8, 114.7, 113.3 (Ar−C, due to accidental overlap only 11 signals are observed), 50.1 (CH_2), 40.5 (NCH_3), 34.5 (SCH), 23.7 (CH_3). MS (ESI): *m*/*z* = 297 [M − Br]$^+$.

Complex *cis*-7a. $Pd(OAc)_2$ (0.112 g, 0.5 mmol) was added to a solution of **5a** (0.299 g, 1 mmol) in CH_3CN (60 mL). The reaction mixture was stirred overnight at 70 °C and then filtered. The solvent of the filtrate was removed *in vacuo*, and the residue was washed several times with CH_2Cl_2, affording a white solid of *cis*-**7a**. Due to insufficient solubility of *cis*-**7a**, the ^{1}H NMR spectrum shows broad signals and the ^{13}C NMR spectrum could not be obtained. *cis*-**7a**, 0.136 g (0.193 mmol), 38% yield. Anal. Calcd for $C_{24}H_{28}Br_2N_4S_2Pd$: C, 41.01; H, 4.02; 7.97. Found: C, 41.10; H, 3.97; N, 8.02. ^{1}H NMR (300 MHz, CD_3CN): δ 7.36−6.82 (m, br, 12 H, Ar−H), 5.45 (brs, 4 H, CH_2), 3.87 (brs, 6 H, NCH_3), 2.55 (brs, 6 H, SCH_3). MS (ESI, positive ions) *m*/*z* (%): 623 (100) [M − Br]$^+$.

Complexes *cis*-7a, *trans-anti*-7a, and *trans-syn*-7a. Ag_2O (0.116 g, 0.5 mmol) was added to a solution of **5a** (0.299 g, 1 mmol) in CH_2Cl_2 (5 mL) and stirred overnight at ambient temperature. The reaction mixture was then filtered and added to a solution of *trans*-[$PdBr_2(CH_3CN)_2$] (0.133 g, 0.5 mmol) in CH_3CN. The suspension was stirred overnight at ambient temperature and filtered to remove AgBr. The volatiles were then removed *in vacuo*, and the residue was washed with diethyl ether. Acetone was added, upon which a yellow precipitate formed upon stirring. The yellow precipitate was filtered, washed with small amounts of acetone, and dried *in vacuo*, affording a mixture of *trans-anti*-**7a** and *trans-syn*-**7a**. The solvent in the acetone filtrate was removed *in vacuo*, and $CHCl_3$ was added to the off-white residue. Upon standing and slow evaporation of $CHCl_3$ *cis*-**7a** precipitates. *cis*-**7a**, 0.157 g (0.223 mmol), 45% yield. *trans-anti*-**7a** + *trans-syn*-**7a**, 0.187 g (0.266 mmol), 53% yield. Anal. Calcd for $C_{24}H_{28}Br_2N_4S_2Pd$: C, 41.01; H, 4.02; 7.97. Found: C, 40.30; H, 4.07; N, 8.00. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59−6.74 (m, 24 H, Ar−H), 5.90 (s, 4 H, CH_2), 5.71 (s, 4 H, CH_2), 4.13 (s, 6 H, NCH_3), 3.99 (s, 6 H, NCH_3), 2.52 (s, 6 H, SCH_3), 2.37 (s, 6 H, SCH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): 169.9 (NCN), 169.8 (NCN), 137.3, 137.1, 134.7, 134.5, 130.5, 130.4, 128.9, 128.7, 126.6, 126.3, 126.1, 125.9 (Ar−C), 122.5, 122.4, 121.2, 121.0 (NCH), 51.6 (CH_2), 51.5 (CH_2), 38.2 (NCH_3), 38.1 (NCH_3), 16.5 (SCH_3), 16.3 (SCH_3). MS (ESI, positive ions) *m*/*z* (%): 623 (100) [M − Br]$^+$.

Complexes *trans-anti*-7b and *trans-syn*-7b. Ag_2O (0.116 g, 0.5 mmol) was added to a solution of **5b** (0.327 g, 1 mmol) in CH_2Cl_2 (5 mL) and stirred overnight at ambient temperature. The reaction mixture was then filtered and added to a solution of *trans*-[$PdBr_2(CH_3CN)_2$] (0.133 g, 0.5 mmol) in CH_3CN. The reaction mixture was stirred overnight at ambient temperature and filtered to remove AgBr. The solvent of the filtrate was removed *in vacuo* and the residue washed with diethyl ether and methanol. *trans-anti*-**7b** selectively crystallized from a CH_2Cl_2 solution. *trans-anti*-**7b** + *trans-syn*-**7b**, 0.207 g (0.273 mmol), 54% yield. Anal. Calcd for $C_{28}H_{36}Br_2N_4S_2Pd$: C, 44.31; H, 4.78; N, 7.38. Found: C, 44.80; H, 4.90; N, 7.36. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61−6.72 (m, 24 H, Ar−H), 6.01 (s, 4 H, CH_2), 5.88 (s, 4 H, CH_2), 4.15 (s, 6 H, NCH_3), 3.99 (s, 6 H, NCH_3), 3.41 (sep, ^3J(H,H) = 6.7 Hz, 2 H, CH), 3.27 (sep, ^3J(H,H) = 6.6 Hz, 2 H, CH), 1.34 (d, ^3J(H,H) = 6.6 Hz, 12 H, CH_3), 1.22 (d, ^3J(H,H) = 6.8 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): 169.8 (NCN), 169.7 (NCN), 138.3, 138.2, 134.4, 134.3, 133.2, 133.1, 130.8, 130.6, 128.5, 128.4, 128.1, 128.0 (Ar−C), 122.6, 121.0 (NCH), 51.9 (CH_2), 51.8 (CH_2), 39.2 (NCH_3), 39.1 (NCH_3), 38.2 (CH), 38.1 (CH), 23.3 (CH_3), 23.2 (CH_3). MS (ESI, positive ions) *m*/*z* (%): 679 (100) [M − Br]$^+$.

Complex *cis*-8a. A mixture of salt **6a** (0.180 g, 0.52 mmol) and $Pd(OAc)_2$ (0.056 g, 0.25 mmol) was dissolved in DMSO (10 mL) and stirred overnight at 90 °C. A clear yellow solution was obtained. The solvent was removed by vacuum distillation, and the resulting residue was dissolved in CH_2Cl_2 (15 mL) and washed with H_2O (4 × 15 mL). Drying of the organic phase over Na_2SO_4 followed by removal of the solvent *in vacuo* gave a yellow solid. Subsequent washing with diethyl ether produced a crystalline yellow powder. Slow evaporation of a saturated acetonitrile solution afforded the product as yellow crystals. *cis*-**8a**, 0.176 g (0.22 mmol), 89% yield. Anal. Calcd for $C_{32}H_{32}Br_2N_4S_2Pd$: C, 47.86; H, 4.02; N, 6.98. Found: C, 48.03; H, 4.07; N, 6.90. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24−6.88 (m, 12 H, Ar−H), 6.26−6.00 (m, 4 H, Ar−H), 6.07 (d, ^2J(H,H) = 17.2 Hz, 2 H, NCH_2), 5.67 (d, ^2J(H,H) = 17.2 Hz, 2 H, NCH_2), 4.08 (s, 6 H, NCH_3), 2.62 (s, 6 H, SCH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 175.1 (NCN), 136.4, 135.6, 134.1, 131.8, 128.9, 125.6, 125.1, 124.3, 124.3, 111.6, 111.2 (Ar−C), 50.0 (NCH_2), 36.5 (NCH_3), 16.2 (SCH_3). MS (ESI): *m*/*z* = 723 [M − Br]$^+$.

Complex *cis*-8b. A mixture of salt **6b** (0.415 g, 1.10 mmol) and $Pd(OAc)_2$ (0.112 g, 0.50 mmol) was dissolved in DMSO (15 mL)

and stirred overnight at 90 °C. The light brown solution turned yellow after a few hours. The reaction mixture was filtered, and the solvent of the filtrate was removed by vacuum distillation. The resulting residue was dissolved in CH_2Cl_2 (30 mL) and washed with H_2O (4 × 20 mL). Drying of the organic phase over Na_2SO_4 followed by removal of the solvent *in vacuo* afforded the compound as a yellow powder. The *cis*-complex was isolated by column chromatography using a ethyl acetate/hexane (5:1) eluting solvent mixture (R_f = 0.32). *cis*-**8b**, 0.286 g (0.33 mmol), 67% yield. Anal. Calcd for $C_{36}H_{40}Br_2N_4S_2Pd$: C, 50.33; H, 4.69; N, 6.52. Found: C, 49.98; H, 4.47; N, 6.40. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 (dd, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 0.8 Hz, 2 H, Ar−H), 7.22−7.17 (m, 2 H, Ar−H), 7.11−6.98 (m, 6 H, Ar−H), 6.82 (d, ^3J(H,H) = 8.0 Hz, 2 H, Ar−H), 6.31 (t, ^3J(H,H) = 7.4 Hz, 2 H, Ar−H), 6.14 (d, ^2J(H,H) = 17.0 Hz, 2 H, NCH_2), 6.05 (d, ^3J(H,H) = 7.5 Hz, 2 H, Ar−H), 5.78 (d, ^2J(H,H) = 17.0 Hz, 2 H, NCH_2), 4.07 (s, 6 H, NCH_3), 3.55 (sep, ^3J(H,H) = 6.6 Hz, 2 H, SCH), 1.42 (d, ^3J(H,H) = 6.7 Hz, 6 H, SCH(CH_3)), 1.40 (d, ^3J(H,H) = 6.6 Hz, 6 H, SCH(CH_3)). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 174.4 (NCN), 135.0, 134.1, 133.5, 133.4, 130.7, 128.1, 126.1, 125.1, 123.6, 123.5, 110.9, 110.4 (Ar−C), 50.0 (NCH_2), 38.1 (NCH_3), 35.8 (SCH), 23.1 (SCH_3), 22.9 (SCH_3). MS (ESI): m/z = 779 [M − Br]$^+$.

Complex 9. Ag_2O (0.116 g, 0.5 mmol) was added to a solution of **5a** (0.299 g, 1 mmol) in CH_2Cl_2 (5 mL) and stirred overnight at ambient temperature. The reaction mixture was then filtered directly into a solution of *trans*-[$PdBr_2(CH_3CN)_2$] (0.266 g, 1 mmol) in CH_3CN. The reaction mixture was stirred overnight at ambient temperature and filtered to remove AgBr. The volatiles were then removed *in vacuo*. The residue was dissolved in CH_3CN and added to a solution of diethyl ether. The suspension was filtered, and the residue was washed with ethyl acetate. Crystals were obtained from the vapor diffusion of diethyl ether into a DMF solution. The ^{1}H NMR spectrum showed broad signals that were not well resolved. ^{13}C NMR was not recorded due to the presence of a complicated product mixture (*vide supra*). **9**, 0.382 g (0.788 mmol), 79% yield. Anal. Calcd for $C_{12}H_{14}Br_2N_4SPd$: C, 29.75; H, 2.91; N, 5.78. Found: C, 29.30; H, 2.47; N, 5.40. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50−6.54 (m, br, 6 H, Ar−H), 5.93 (brs, 2 H, CH_2), 4.04 (brs, 3 H, NCH_3), 2.83 (brs, 3 H, SCH_3).

Complex 10. PPh_3 (0.077 g, 0.29 mmol) was added to a solution of **9** (0.129 g, 0.27 mmol) in CH_3CN (5 mL). The reaction mixture was stirred for 0.5 h at ambient temperature. The volatiles were then removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and the mixture was filtered. The solvent of the filtrate was removed and the residue washed with small amounts of acetone. Upon drying *in vacuo*, complex **10** was isolated as a yellow powder. **10**, 0.129 g (0.173 mmol), 64% yield. Anal. Calcd for $C_{30}H_{29}Br_2N_2PSPd$: C, 48.25; H, 3.91; N, 3.75. Found: C, 48.30; H, 3.97; N, 3.69. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66−7.05 (m, 19 H, Ar−H), 6.56 (d, ^3J(H,H) = 1.9 Hz, 1 H, CH_{Imd}), 6.40 (d, ^3J(H,H) = 1.9 Hz, 1 H, CH_{Imd}), 5.76 (d, ^2J(H,H) = 14.3 Hz, 1 H, C*H*H), 4.71 (d, ^2J(H,H) = 14.3 Hz, 1 H, CH*H*), 3.61 (s, 3 H, NCH_3), 2.42 (s, 3 H, SCH_3). ^{31}P NMR (121 MHz, $CDCl_3$): δ 27.1 (s, PPh_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 162.7 (NCN), 137.5 (Ar−C), 134.3 (d, J(P,C) = 11.0 Hz, Ar−C), 132.3 (Ar−C), 131.2 (d, ^1J(P,C) = 35.7, Ar−C), 131.0 (d, ^4J(P,C) = 2.7 Hz, Ar−C), 130.2, 129.5 (Ar−C), 128.5 (d, $^{2/3}J$(P,C) = 11.0 Hz, Ar−C), 126.7, 126.3, 122.8, 121.3 (Ar−C), 51.4 (CH_2), 37.9 (NCH_3), 16.4 (SCH_3). MS (ESI, positive ions) m/z (%): 667 (100) [M − Br]$^+$.

General Procedure for the Suzuki−Miyaura Coupling. In a typical run, a test tube was charged with a mixture of aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), potassium carbonate (2 mmol), precatalyst, and [$N(n$-$C_4H_9)_4$]Br (1.5 mmol) (for entries 11−25 in Table 1). To the mixture was added H_2O (3 mL). The reaction mixture was vigorously stirred at the appropriate temperature (RT or 85 °C). After the desired reaction time, the solution was allowed to cool. Then 10 mL of dichloromethane was added to the reaction mixture, and the organic phase was extracted with water (6 × 5 mL) and dried over $MgSO_4$. The solvent was removed by evaporation to give a crude product, which was analyzed by ^{1}H NMR spectroscopy.

X-ray Diffraction Studies. X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation with the SMART suite of programs.[20] Data were processed and corrected for Lorentz and polarization effects with SAINT[21] and for absorption effect with SADABS.[22] Structural solution and refinement were carried out with the SHELXTL suite of programs.[23] 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 the most important crystallographic data is given in the Supporting Information. CCDC-610655−610657 contain the supplementary crystallographic data for complexes **9**, **10**, and *cis*-**7a**·2DMF.[12] These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgment. We thank the National University of Singapore for financial support (Grant No. R 143-000-327-133) and the CMMAC staff of our department for technical assistance.

Supporting Information Available: Crystallographic data for *cis*-**7a**·2DMF, *trans-anti*-**7b**, *cis*-**8a**, *trans-anti*-**8b**, **9**, and **10** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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