5614 *Organometallics* **2010,** *29,* 5614–5626
DOI: 10.1021/om100500y

ORGANOMETALLICS
Article

Thioether-Functionalized N-Heterocyclic Carbenes: Mono- and Bis-(S,C_{NHC}) Palladium Complexes, Catalytic C−C Coupling, and Characterization of a Unique $Ag_4I_4(S,C_{NHC})_2$ Planar Cluster†

Christophe Fliedel and Pierre Braunstein*

Laboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), Université de Strasbourg, 4 Rue Blaise Pascal, F-67081 Strasbourg Cedex, France

Received May 21, 2010

We report a one-step synthesis for new *N*-aryl-*N*′-thioether imidazolium salts that are precursors to (S,C_{NHC}) ligands in N-heterocyclic carbene (NHC) complexes. The crystal structure of the *N*-(2,6-diisopropylphenyl)-*N*′-ethyl-(ethyl)-sulfide imidazolium hexafluorophosphate **8**·HPF_6 was determined by X-ray diffraction and revealed H-bonding interactions between the PF_6 anion and, in particular, the imidazolium 2-H proton. The corresponding Ag(I) NHC complexes **1**·AgX−**8**·AgX were synthesized and fully characterized. An unprecedented planar, centrosymmetric cluster, [$Ag_4(\mu_3\text{-}I)_2(\mu_2\text{-}I)_2(\mu_2\text{-}S,C_{NHC})_2$] [**5**·$(AgI)_2]_2$, was obtained in which two functional carbene ligands bridge two edges of a silver rectangle. With the *N*-alkyl-*N*′-thioether ligands, [$PdCl_2(S,C_{NHC})_2$] complexes were prepared by two different routes: the usual transmetalation reaction involving the Ag(I) NHC reagent or a stepwise sequence involving deprotonation of the imidazolium function in zwitterionic intermediates where the thioether function is bound to the Pd(II) center. The crystal structures of two representative complexes, **10** and **12**, with an ethyl- or a phenyl-thioether function, respectively, coordinated to the Pd(II) center, have been determined by X-ray diffraction and confirmed their mononuclear structure. In the neutral complexes *trans*-[$PdCl_2(C_{NHC})_2$] (**17**−**20**) the thioether group is not coordinated to the metal center, as also confirmed by the crystal structure determination by X-ray diffraction of the bis-NHC Pd(II) dichloro complex **18**, which also established the *trans-anti* arrangement of the ligands. The first examples of bis-chelated dicationic palladium(II) complexes with thioether-functionalized NHCs, [$Pd(S,C_{NHC})_2][BF_4]_2$ (**21**−**24**), are reported, which were selectively obtained with a *cis* arrangement of the ligands. The Pd(II) complexes **9**−**24** were evaluated in Suzuki−Miyaura cross-coupling reactions under various conditions, and a higher catalytic activity was observed for the complexes in which the sulfur atom is coordinated to the metal center.

Introduction

N-Heterocyclic carbenes (NHCs) have attracted increasing attention in organometallic chemistry since the pioneering work of Lappert,[1] the report of the first stable free carbene,[2] the synthesis of various silver-NHC complexes,[3] and the report of their use as carbene transfer reagents.[4] Metal-NHC complexes have already found many applications in homogeneous catalysis.[5] NHCs are often used as phosphine alternatives owing to their better stability toward oxidation and the formation of more stable metal complexes.[6] For cross-coupling reactions, strong σ-donor ligands are necessary and the NHCs are the only class of ligands able to challenge the long-used tertiary phosphines.[7] Although the association of NHCs with palladium(II) precursors has been extensively studied in catalysis[8] and NHC-Pd complexes compared to phosphine-Pd catalysts,[9] the use of well-defined NHC-Pd(II) complexes as precatalysts for cross-coupling reactions remains underdeveloped.[10]

† Part of the Dietmar Seyferth Festschrift. Dedicated to Prof. Dietmar Seyferth for his outstanding career dedicated to all aspects of organometallic chemistry: research, teaching, and publishing.

*Corresponding author. E-mail: braunstein@unistra.fr. Fax: +33 368 851 322. Tel: +33 368 851 308.

(1) (a) Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185. (b) Lappert, M. F. *J. Organomet. Chem.* **2005**, *690*, 5467.

(2) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.

(3) (a) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. *Chem. Rev.* **2009**, *109*, 3561. (b) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122. (c) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405.

(4) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.

(5) (a) de Frémont, P.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862. (b) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122. (c) Hahn, F. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1348. (d) Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815. (e) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, 619. (f) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (g) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.

(6) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2000**, *46*, 181.

(7) (a) Miura, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2201. (b) Gillespie, J. A.; Dodds, D. L.; Kamer, P. C. J. *Dalton Trans.* **2010**, *39*, 2751.

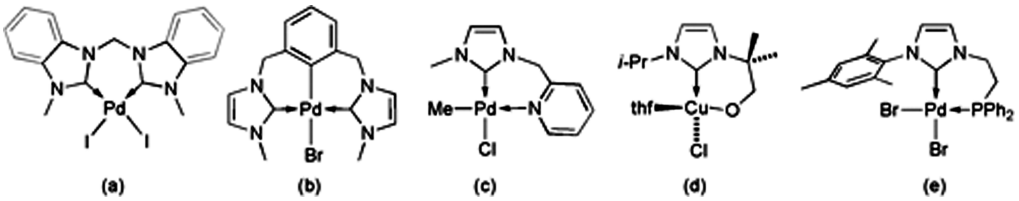
(8) (a) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768. (b) Díez-González, S.; Nolan, S. P. *Top. Organomet. Chem.* **2007**, *21*, 47.

(9) See e.g.: Fliedel, C.; Maisse-François, A.; Bellemin-Laponnaz, S. *Inorg. Chim. Acta* **2007**, *360*, 143.

(10) Marion, N.; Nolan, S. P. *Acc. Chem. Res.* **2008**, *41*, 1440.

 Published on Web 08/24/2010

Chart 1. Examples of (a) Single-Atom-Bridged Bis(C_{NHC}),[12o,q] (b) Phenylene-Bridged Bis(C_{NHC}),[12n] (c) *N*-,[13g] (d) *O*-,[14e] and (e) *P*,C_{NHC}[15j] Metal Complexes



The number of bis- and, more generally, polydentate NHC-containing ligands has grown very rapidly.[11] Varying the nature of the linker between the donor functions and/or the nature of the latter allows the creation of diversified families of ligands. Examples of complexes containing two carbene donors linked through a single atom or a pyridine or phenylene backbone have been described (Chart 1, a and b).[12] The synthesis of functional NHCs associating a carbene ligand with a chemically different donor function has given rise to the formation of *N*-,[13] *O*-,[14] and *P*,C_{NHC}[15] metal complexes (Chart 1, c−e). These complexes rapidly showed great potential in homogeneous catalysis.[5f,8a,16] The chelating ability of these ligands resulted in the formation of highly stable complexes with a strong σ-donor function (NHC) and a more labile one, which could result in a hemilabile behavior of the resulting systems in solution.[17] In turn, this could lead to the temporary dissociation of the heteroatom donor from the metal during a catalytic cycle, allowing the coordination of a substrate, its metal-assisted transformation, and, after product elimination, stabilizing recoordination of this function.

Although the presence of a sulfur atom in the side chain attached to nitrogen has revealed to be beneficial for some catalytic reactions, e.g., catalytic Mizoroki−Heck coupling, ketone hydrosilylation, or allylic substitution reactions,[18,19] only a few *S*,C_{NHC} metal complexes have been described until now. Examples of mono(thioether) imidazolium[18] and bis(thioether) imidazolium salts[19] and *S*,C_{NHC} complexes obtained by oxidative addition of a carbon sulfur bond across a zerovalent metal precursor have been reported (Chart 2).[20]

We recently reported an atom-efficient, one-step, and solvent-free synthesis of new *S*,C_{NHC} precursors bearing a thioether function on a nitrogen atom, together with their Ag(I) and Pd(II) complexes.[18e] In light of preliminary catalytic results obtained with the latter, we decided to extend our investigations on this ligand class. Here, we report the synthesis of monocarbene chelate complexes [$PdCl_2$(*S*,C_{NHC})] by transmetalation

(11) (a) Flores-Figueroa, A.; Pape, T.; Feldmann, K.-O.; Hahn, F. E. *Chem. Commun.* **2010**, *46*, 324. (b) Kaufhold, O.; Stasch, A.; Pape, T.; Hepp, A.; Edwards, P. G.; Newman, P. D.; Hahn, F. E. *J. Am. Chem. Soc.* **2009**, *131*, 306. (c) Flores-Figueroa, A.; Kaufhold, O.; Hepp, A.; Fröhlich, R.; Hahn, F. E. *Organometallics* **2009**, *28*, 6362. (d) Mata, J. A.; Poyatos, M.; Peris, E. *Coord. Chem. Rev.* **2007**, *251*, 841. (e) Pugh, D.; Danopoulos, A. A. *Coord. Chem. Rev.* **2007**, *251*, 610. (f) Kaufhold, O.; Stasch, A.; Edwards, P. G.; Hahn, F. E. *Chem. Commun.* **2007**, 1822.

(12) (a) Huynh, H. V.; Jothibasu, R. *Eur. J. Inorg. Chem.* **2009**, 1926. (b) Hahn, F. E.; Jahnke, M. C.; Pape, T. *Organometallics* **2007**, *26*, 150. (c) Nielsen, D. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2006**, *359*, 1855. (d) Pugh, D.; Wright, J. A.; Freeman, S.; Danopoulos, A. A. *Dalton Trans.* **2006**, 775. (e) Danopoulos, A. A.; Wright, J. A.; Motherwell, W. B.; Ellwood, S. *Organometallics* **2004**, *23*, 4807. (f) Hahn, F. E.; Jahnke, M. C.; Gomez-Benitez, V.; Morales-Morales, D.; Pape, T. *Organometallics* **2005**, *24*, 6458. (g) McGuinness, D. S.; Gibson, V. C.; Steed, J. W. *Organometallics* **2004**, *23*, 6288. (h) Danopoulos, A. A.; Tulloch, A. A. D.; Winston, S.; Eastham, G.; Hursthouse, M. B. *Dalton Trans.* **2003**, 1009. (i) Miecznikowski, J. R.; Gründemann, S.; Albrecht, M.; Megret, C.; Clot, E.; Faller, J. W.; Eisenstein, O.; Crabtree, R. H. *Dalton Trans.* **2003**, 831. (j) Poyatos, M.; Mata, J. A.; Falomir, E.; Crabtree, R. H.; Peris, E. *Organometallics* **2003**, *22*, 1110. (k) Simons, R. S.; Custer, P.; Tessier, C. A.; Youngs, W. J. *Organometallics* **2003**, *22*, 1979. (l) Loch, J. A.; Albrecht, M.; Peris, E.; Mata, J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 700. (m) Nielsen, D. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2002**, *327*, 116. (n) Peris, E.; Loch, J. A.; Mata, J.; Crabtree, R. H. *Chem. Commun.* **2001**, 201. (o) Tulloch, A. A. D.; Danopoulos, A. A.; Tizzard, G. J.; Coles, S. J.; Hursthouse, M. B.; Hay-Motherwell, R. S.; Motherwell, W. B. *Chem. Commun.* **2001**, 1270. (p) Gründemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2001**, *20*, 5485. (q) Hahn, F. E.; Foth, M. *J. Organomet. Chem.* **1999**, *585*, 241. (r) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371.

(13) (a) Jahnke, M. C.; Pape, T.; Hahn, F. E. *Eur. J. Inorg. Chem.* **2009**, 1960. (b) Jiménez, M. V.; Pérez-Torrente, J. J.; Bartolomé, M. I.; Gierz, V.; Lahoz, F. J.; Oro, L. A. *Organometallics* **2008**, *27*, 224. (c) Danopoulos, A. A.; Tsoureas, N.; Macgregor, S. A.; Smith, C. *Organometallics* **2007**, *26*, 253. (d) Stylianides, N.; Danopoulos, A. A.; Tsoureas, N. *J. Organomet. Chem.* **2005**, *690*, 5948. (e) Gade, L. H.; César, V.; Bellemin-Laponnaz, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1014. (f) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Organometallics* **2002**, *21*, 5204. (g) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741.

(14) (a) Jones, N. A.; Liddle, S. T.; Wilson, C.; Arnold, P. L. *Organometallics* **2007**, *26*, 755. (b) Arnold, P. L.; Rodden, M.; Wilson, C. *Chem. Commun.* **2005**, 1743. (c) Clavier, H.; Coutable, L.; Toupet, L.; Guillemin, J. C.; Mauduit, M. *J. Organomet. Chem.* **2005**, *690*, 5237. (d) Arnold, P. L.; Blake, A. J.; Wilson, C. *Chem.—Eur. J.* **2005**, *11*, 6095. (e) Arnold, P. L.; Rodden, M.; Davis, K. M.; Scarisbrick, A. C.; Blake, A. J. *Chem. Commun.* **2004**, 1612. (f) Waltman, A. W.; Grubbs, R. H. *Organometallics* **2004**, *23*, 3105. (g) Arnold, P. L.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2001**, 2340.

(15) (a) Danopoulos, A. A.; Tsoureas, N.; Macgregor, S. A.; Smith, C. *Organometallics* **2007**, *26*, 253. (b) Lee, C. C.; Ke, W. C.; Chan, K. T.; Lai, C. L.; Hu, C. H.; Lee, H. M. *Chem.—Eur. J.* **2007**, *13*, 582. (c) Wolf, J.; Labande, A.; Daran, J. C.; Poli, R. *J. Organomet. Chem.* **2006**, *691*, 433. (d) Hahn, F. E.; Jahnke, M. C.; Pape, T. *Organometallics* **2006**, *25*, 5927. (e) Zeng, J. Y.; Hsieh, M.-H.; Lee, H. M. *J. Organomet. Chem.* **2005**, *690*, 5662. (f) Field, L. D.; Messerle, B. A.; Vuong, K. Q.; Turner, P. *Organometallics* **2005**, *24*, 4241. (g) Chiu, P. L.; Lee, H. M. *Organometallics* **2005**, *24*, 1692. (h) Lee, H. M.; Zeng, J. Y.; Hu, C.-H.; Lee, M.-T. *Inorg. Chem.* **2004**, *43*, 6822. (i) Yang, C.; Lee, H. M.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1511. (j) Tsoureas, N.; Danopoulos, A. A.; Tulloch, A. A. D.; Light, M. E. *Organometallics* **2003**, *22*, 4750.

(16) Normand, A. T.; Cavell, K. J. *Eur. J. Inorg. Chem.* **2008**, 2781.

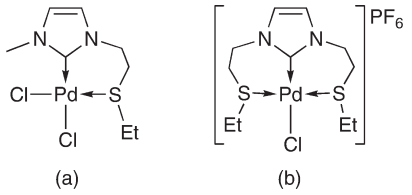
(17) (a) Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 680. (b) Braunstein, P. *J. Organomet. Chem.* **2004**, *689*, 3953.

(18) (a) Huynh, H. V.; Chew, Y. X. *Inorg. Chim. Acta* **2010**, *363*, 1979. (b) Liu, S. T.; Lee, C.-I.; Fu, C.-F.; Chen, C.-H.; Liu, Y.-H.; Elsevier, C. J.; Peng, S.-M.; Chen, J.-T. *Organometallics* **2009**, *28*, 6957. (c) Huynh, H. V.; Yuan, D.; Han, Y. *Dalton Trans.* **2009**, 7262. (d) Gandolfi, C.; Heckenroth, M.; Neels, A.; Laurenczy, G.; Albrecht, M. *Organometallics* **2009**, *28*, 5112. (e) Fliedel, C.; Schnee, G.; Braunstein, P. *Dalton Trans.* **2009**, 2474. (f) McGuinness, D. S.; Suttil, J. A.; Gardiner, M. G.; Davies, N. W. *Organometallics* **2008**, *27*, 4238. (g) Roseblade, S. J.; Ros, A.; Monge, D.; Alcarazo, M.; Alvarez, E.; Lassaletta, J. M.; Fernandez, R. *Organometallics* **2007**, *26*, 2570. (h) Wolf, J.; Labande, A.; Daran, J.-C.; Poli, R. *Eur. J. Inorg. Chem.* **2007**, 5069. (i) Huynh, H. V.; Yeo, C. H.; Tan, G. K. *Chem. Commun.* **2006**, 3833. (j) Ros, A.; Monge, D.; Alcarazo, M.; Alvarez, E.; Lassaletta, J. M.; Fernandez, R. *Organometallics* **2006**, *25*, 6039. (k) Seo, H.; Park, H. J.; Kim, B. Y.; Lee, J. H.; Son, S. U.; Chung, Y. K. *Organometallics* **2003**, *22*, 618. (l) Matsumura, N.; Kawano, J.-I.; Fukunishi, N.; Inoue, H.; Yasui, M.; Iwasaki, F. *J. Am. Chem. Soc.* **1995**, *117*, 3623. (m) Sellmann, D.; Prechtel, W.; Knoch, F.; Moll, M. *Organometallics* **1992**, *11*, 2346.

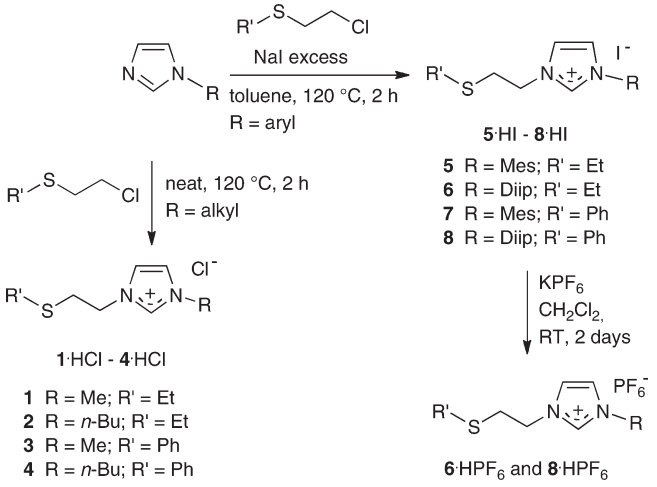
(19) (a) Fliedel, C.; Sabbatini, A.; Braunstein, P. *Dalton Trans.* **2010**, DOI: 10.1039/c0dt00351d. (b) Iglesias-Sigüenza, J.; Ros, A.; Diez, E.; Magriz, A.; Vazquez, A.; Alvarez, E.; Fernandez, R.; Lassaletta, J. M. *Dalton Trans.* **2009**, 8485.

(20) (a) Cabeza, J. A.; Silva, I. D.; del Rio, I.; Sanchez-Vega, M. G. *Dalton Trans.* **2006**, 3966. (b) Cabeza, J. A.; del Rio, I.; Sanchez-Vega, M. G.; Suarez, M. *Organometallics* **2006**, *25*, 1831.

Chart 2. Examples of (a) Chelate S,C_{NHC}[18e] and (b) Pincer S,C_{NHC},S[19a] Palladium(II) Complexes



Scheme 1. Synthesis of the Carbene Precursors



reaction or by an alternative pathway involving zwitterionic intermediates where the functional imidazolium ligand is first coordinated to the metal though its thioether function and then deprotonated at the imidazolium site by a weak base. We also prepared bis-carbene complexes $[PdCl_2(C_{NHC})_2]$ in which the sulfur atom remains uncoordinated and *C*,*S*-bis-chelated dicationic species $[Pd(S,C_{NHC})_2][BF_4]_2$, attractive for catalysis owing to a potentially easily accessible vacant coordination site produced by displacement of the sulfur donors. Since we could not isolate the corresponding free carbenes, their thione derivatives were prepared in order to show that the imidazolium salts can be deprotonated by an external base. We then extended this family of ligands to aryl thioether imidazolium salts to modify the physical properties, solubility, and steric and electronic characteristics of the resulting complexes. The corresponding silver(I) complexes were synthesized, and the structure of a unique $[Ag_4I_4(S,C_{NHC})_2]$ planar cluster is reported.

Results and Discussion

Preparation of the Carbene Precursors. The *N*-alkyl-*N*′-thioether imidazolium chlorides **1**·HCl−**4**·HCl were prepared as described previously (Scheme 1).[18e] This procedure was slightly modified for the preparation of the *N*-aryl-*N*′-thioether imidazolium salts. The solid reagents, *N*-(2,4,6-trimethylphenyl)- and *N*-(2,6-diisopropylphenyl)imidazole, were dissolved in toluene, and addition of excess NaI favored the reaction with 2-chloroethyl ethylsulfide or 2-chloroethyl phenylsulfide. This reaction resulted at the same time in a counteranion exchange, which afforded the *N*-aryl-*N*′-thioether imidazolium iodides **5**·HI−**8**·HI (Scheme 1). This anion exchange and the electronic effect of the aryl substituents resulted in an upfield shift for the 2-H protons of **5**·HI−**8**·HI between 9.26 and 9.78 ppm compared to **1**·HCl−**4**·HCl, for which the 2-H proton signal appears between 10.36 and 10.51 ppm. The $^{13}C\{^1H\}$ NMR resonances of the N*C*N carbons between 137.2 and 137.8 ppm were also affected. Whereas the corresponding bromide salt **5**·HBr has been previously described,[18h] its synthesis involved first that of the *N*-(2-bromoethyl)-*N*′-(2,4,6-trimethylphenyl)-imidazolium bromide, in two steps, with an overall yield of 60%.[21]

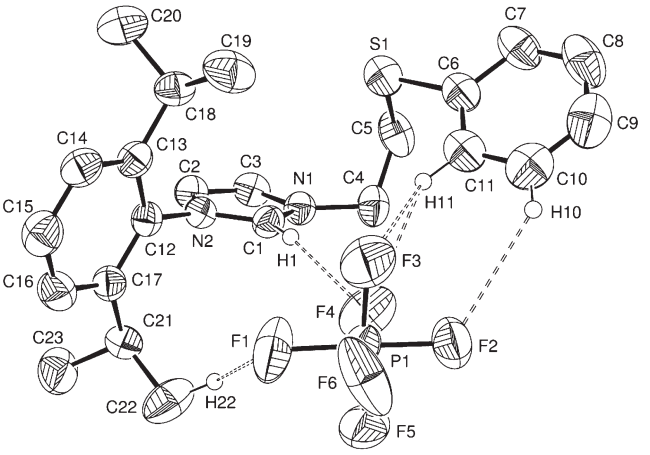


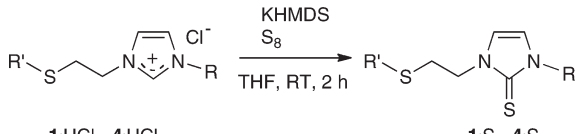
Figure 1. View of the molecular structure of **8**·HPF_6. Only the hydrogen atoms involved in H-bonding are shown for clarity. Ellipsoids are represented at the 50% probability level. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): C1−N1 1.319(3), C1−N2 1.328(3), C1−H1 0.95(2), H1−F4 2.200(2), C10−F2 3.527(5), C11−F3 3.340(1), C11−F4 3.460(1), C22−F1 3.421(3), N1−C1−N2 109.24(19), N1−C4−C5 110.4(2), C14−C13−N2 117.5(2), C1−N1−C4−C5 105.9(3), C1−N2−C12−C13 81.4(3).

Reaction of the *N*-(2,6-diisopropylphenyl)-substituted imidazolium iodides with excess KPF_6 at room temperature in CH_2Cl_2 for 2 days resulted in their quantitative conversion to the hexafluorophosphate salts **6**·HPF_6 and **8**·HPF_6. Consistent with the anion exchange, an upfield shift was observed in their ^1H NMR spectra for the 2-H resonances at 9.04 and 8.68 ppm and in the $^{13}C\{^1H\}$ NMR spectra for the N*C*N carbons at 136.0 and 135.1 ppm, respectively. Single crystals of **8**·HPF_6 suitable for X-ray diffraction studies were obtained by slow diffusion of pentane into a saturated dichloromethane solution of **8**·HPF_6. Its molecular structure is depicted in Figure 1. The aromatic substituent at N2 is almost orthogonal to the NCN ring, the angle between the 2,6-diisopropylphenyl and the imidazole rings being 84.2°. The steric constraints are also minimized on the N1 side with a torsion angle C1−N1−C4−C5 of 105.9° and an angle between the N1−C4−C5 plane and the imidazole ring of 70.0°. In the solid state, nonclassical hydrogen bonds exist between the imidazolium and the PF_6 counteranion. The strongest one is between the acidic hydrogen H1 and the fluorine atom F4 (2.20 Å). The orientation of the phenyl ring from the thioether moiety is probably also influenced by the three nonclassical H bonds between their hydrogen atoms H11 and H12 and the fluorine atoms F2, F3, and F4 (see values below).

Synthesis of the Thione Derivatives. The free carbenes **1**−**4** could not be isolated, owing to their low stability in solution, but addition of sulfur to the reaction mixture yielded the corresponding thiones **1**·S−**4**·S, respectively, which could be isolated and characterized (Scheme 2). Deprotonation of the imidazolium salts was established by the disappearance of the 2-H

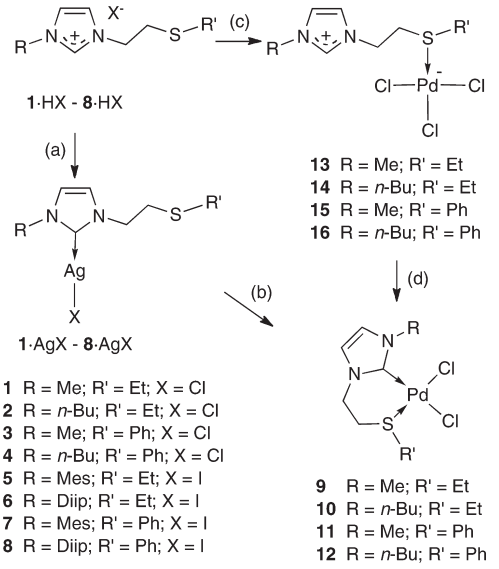
(21) Wolf, J.; Labande, A.; Natella, M.; Daran, J.-C.; Poli, R. *J. Mol. Catal. A* **2009**, *259*, 205.

Scheme 2. Synthesis of the Thione Derivatives of the NHC, 1·S−4·S



1 R = Me; R' = Et
2 R = *n*-Bu; R' = Et
3 R = Me; R' = Ph
4 R = *n*-Bu; R' = Ph

Scheme 3. Two Pathways for the Synthesis of [$PdCl_2(S,C_{NHC})$] Complexes[a]



1 R = Me; R' = Et; X = Cl
2 R = *n*-Bu; R' = Et; X = Cl
3 R = Me; R' = Ph; X = Cl
4 R = *n*-Bu; R' = Ph; X = Cl
5 R = Mes; R' = Et; X = I
6 R = Diip; R' = Et; X = I
7 R = Mes; R' = Ph; X = I
8 R = Diip; R' = Ph; X = I

13 R = Me; R' = Et
14 R = *n*-Bu; R' = Et
15 R = Me; R' = Ph
16 R = *n*-Bu; R' = Ph

9 R = Me; R' = Et
10 R = *n*-Bu; R' = Et
11 R = Me; R' = Ph
12 R = *n*-Bu; R' = Ph

[a] Conditions: (a): 1 equiv Ag_2O, CH_2Cl_2, RT; (b): 1 equiv [$PdCl_2$-(cod)], CH_2Cl_2, RT; (c): 1 equiv [$PdCl_2$(cod)], CH_2Cl_2, RT; (d): 1 equiv Cs_2CO_3, MeCN, 60 °C.

imidazolium ^{1}H NMR resonance. The $^{13}C\{^1H\}$ NMR spectra of these thiones showed a typical downfield shift for the N*C*N carbon signal between 161.6 and 162.1 ppm. The ESI-MS spectra and the elemental analysis confirmed the C=S bond formation. By comparison with the IR spectra of the corresponding imidazolium salts, the C=S stretching vibration of the thiones **1**·S−**4**·S is tentatively assigned to an intense absorption in the region 1225−1230 cm^{-1}.

Synthesis of the Silver(I) Complexes. Formation of NHC metal complexes by transmetalation from the corresponding silver carbene complexes represents a well-known procedure.[4] Before using these complexes *in situ* as transmetalation reagents, we attempted to isolate and fully characterize them. Reaction of the imidazolium salts, in CH_2Cl_2 at room temperature, with excess Ag_2O as a base resulted in the formation of the corresponding Ag(I) NHC complexes formulated as **1**·AgCl−**4**·AgCl on the basis of mass spectrometry data (Scheme 3).[18e] The same procedure was followed for the formation of **5**·AgI−**8**·AgI. The success of the reaction is shown by the disappearance of the 2-H proton resonance in the ^{1}H NMR spectra of the complexes. Their formation was also established by a characteristic downfield shift of the N*C*N $^{13}C\{^1H\}$ NMR resonance between 181.5 and 183.3 ppm. The reaction of Ag_2O with the hexafluorophosphate imidazolium salts did not lead to complete conversion. This could be due to strong interactions between the 2-H imidazolium proton and the counteranion (Figure 1), which may

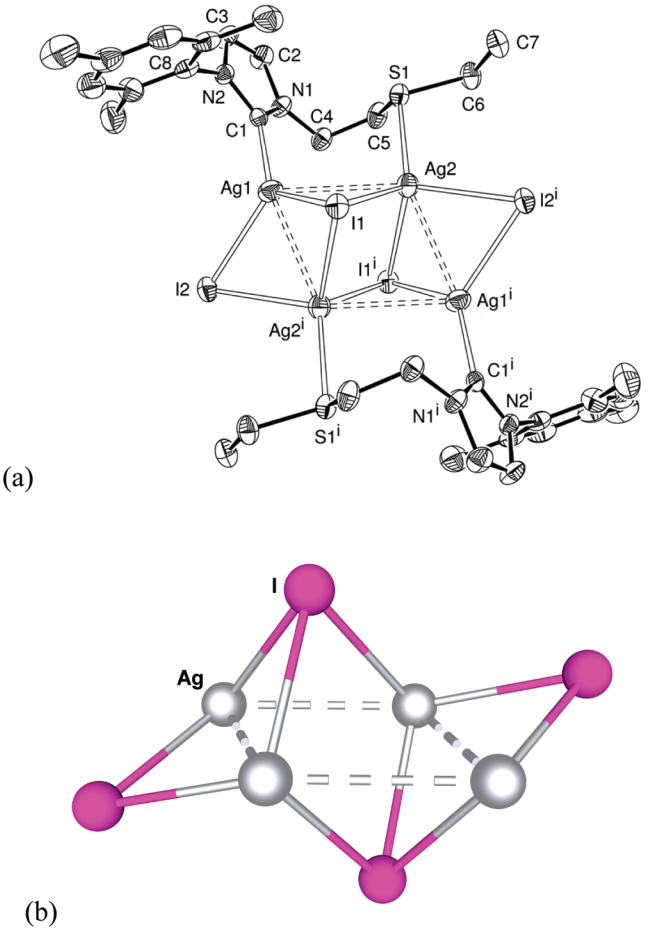


Figure 2. (a) View of the molecular structure of [**5**·$(AgI)_2]_2$. Hydrogen atoms are omitted for clarity. Ellipsoids are represented at the 30% probability level. Selected bond lengths (Å) and bond angles (deg): Ag1−C1 2.128(1), Ag2−S1 2.552(3), Ag1−Ag2 3.219(2), Ag1−Ag2i 2.9657(18), Ag1−I1 2.8259(17), Ag1−I2 2.790(2), Ag2−I1 2.8826(19), Ag2−I2i 2.8423(18), Ag1−I1i 2.953(2), C1−Ag1−I1 128.7(2), C1−Ag1−I2 122.4(2), I1−Ag1−I2 108.07(5), S1−Ag2−I1 121.42(6), S1−Ag2−I1i 110.92(6), S1−Ag2−I2i 109.74(7), Ag1 −Ag2−Ag1i 110.43(5). (b) Simplified view of the Ag_4I_4 core. Color code: gray, silver; pink, iodine.

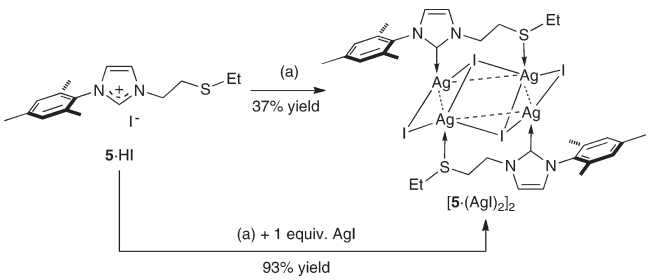
partially prevent deprotonation for steric reasons. In the following experiments involving the [AgX(NHC)] complexes, these will be prepared *in situ* and used as transmetalation agents, after filtration of their solution through a Celite pad to remove unreacted silver oxide.

Slow diffusion of pentane into a saturated dichloromethane solution obtained by reaction of **5**·HI and Ag_2O afforded colorless single crystals suitable for X-ray diffraction and a brownish oil. The crystals were found to correspond to the formulation [$Ag_2(\mu_3$-I)$(\mu_2$-I)$(\mu_2$-$S,C_{NHC})]_2$. Its solid-state molecular structure is depicted in Figure 2 and exhibits an unexpected arrangement (Scheme 4).

Although the coordination chemistry of NHCs toward silver salts is very diversified,[3a,22] the centrosymmetric structure of this polynuclear complex shows an unprecedented planar Ag_4 *core* with two bridging S,C_{NHC} ligands. The two chemically different Ag atoms have different coordination geometries: Ag1 has a slightly distorted trigonal-planar

(22) (a) Lin, I. J. B.; Vasam, C. S. *Coord. Chem. Rev.* **2007**, *251*, 642. (b) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978.

Scheme 4. Preparation of the Planar Cluster $[5\cdot(AgI)_2]_2$[a]



[a] Conditions: (a): 1 equiv Ag_2O, CH_2Cl_2, RT.

geometry formed by C1, I1, and I2, whereas Ag2 has a slightly distorted tetrahedral coordination geometry formed by S1, I1, I1′, and I2′. The angles involving the capping iodides deviate significantly from those in a regular coordination environment [see, e.g., C1−Ag1−I1 = 128.7(2)° and S1−Ag2−I1 = 121.42(6)°]. The distances between the silver atoms supported by the bridging S,C_{NHC} ligand are significantly longer than that between the silver atoms doubly bridged by iodide ligands; Ag1−Ag2 = 3.219(2) Å and Ag1−Ag2′ = 2.9657(18) Å, respectively. The two iodide ligands have different coordination modes, since I2 acts as a μ_2-bridging ligand, supporting the Ag1···Ag2′ interaction, whereas I1 is μ_3-capping three metal centers (Ag1, Ag2, and Ag2′). The Ag···Ag distances [2.9657(18) and 3.219(2) Å] are notably shorter than those in the only other structurally characterized related Ag_4I_4 cluster (to the best of our knowledge), which contains phosphine ligands [Ag···Ag 3.0953(13) and 3.4378(21) Å].[23] The carbene−silver bond length of 2.128(1) Å is in agreement with literature values, and the S−Ag distance is slightly longer than those observed for other donor groups (such as N- or P-donors) in functional NHC complexes.[24] The far-infrared spectrum of crystalline $[5\cdot(AgI)_2]_2$ exhibits strong absorptions at 236 and 154 cm^{-1}, which are tentatively assigned to the stretching vibrations of the μ_2-bridging and μ_3-capping iodides, respectively.

The Ag/I/NHC stoichiometry of 2:2:1 in $[5\cdot(AgI)_2]_2$ differs from that of the reagents (1:1:1). This observation explains why the yield of the formation of this cluster was less than 50%. When the reaction was carried out with an additional equivalent of AgI, the cluster $[5\cdot(AgI)_2]_2$ was formed in 93% yield (Scheme 4).

Synthesis of the Mono-NHC Palladium(II) Complexes. Two routes were investigated for the formation of $[PdCl_2(S,C_{NHC})]$ complexes.

Route A: Transmetalation Reaction (Scheme 3, a and b). This classical method involves the *in situ* synthesis of the corresponding silver complexes **1**·AgCl−**4**·AgCl and their reaction with the palladium precursor, $[PdCl_2(cod)]$ (cod = 1,5-cyclooctadiene), in a 1:1 ratio, to give the desired chelate complexes $[PdCl_2(S,C_{NHC})]$ (**9**−**12**), as reported recently for **9**.[18e]

Route B: *In Situ* Deprotonation of a Zwitterionic Intermediate (Scheme 3, c and d). Our motivation to explore an alternative route was to establish the possible beneficial effect of the presence of the sulfur atom on complex formation under mild conditions and to avoid the use of Ag(I) intermediates, which may interfere in subsequent catalytic reactions. Addition of $[PdCl_2(cod)]$ to a stirred dichloromethane solution of the imidazolium salts **1**·HCl−**4**·HCl led to the displacement of the cod ligand and coordination of the thioether function. The pure product precipitated rapidly, affording complexes **13**−**16** in good yields after washing the solids with pentane to eliminate the traces of cod. The coordination sphere of the palladium atom comprised three Cl and one thioether ligand, and the resulting zwitterionic structure was confirmed spectroscopically. The characteristic signal for the 2H-imidazolium proton is present in the ^1H NMR spectra of all complexes between 9.10 and 9.23 ppm. The ESI-MS spectra reveal as most intense peaks the $[M + Na]^+$ and $[M - Cl]^+$ ions, with the expected isotopic distributions, which rules out a hypothetical ion-pair structure of general formula $[(L\cdot H)_2(PdCl_4)]$ (**L** = carbene **1**−**4**). The far-infrared spectra of the complexes **13**−**16** showed a typical pattern for the ν(Pd−Cl) vibrations of a $LPdCl_3$ fragment.[25] The elemental analyses of these complexes were also in good agreement with the calculated values. Owing to the low solubility of these compounds in organic solvents, characteristic for highly polar compounds, no $^{13}C\{^1H\}$ NMR spectra could be recorded for complexes **13**−**15** and the N*C*N signal was not observed in the spectrum of **16**. These Pd(II) complexes are not air-, light-, or moisture-sensitive and can be stored for weeks without any trace of degradation, in contrast to most silver NHC complexes. This pathway thus allows a stepwise and easy access to catalyst precursors, which could be immediately employed in catalysis. We thus examined the formation of chelate species by deprotonation of the zwitterionic complexes **13**−**16** for 3 h with one equivalent of the weak base Cs_2CO_3 in refluxing acetonitrile. This afforded the desired complexes of general formula $[PdCl_2(S,C_{NHC})]$ (**9**−**12**), respectively. All the spectroscopic data confirm their mononuclear structure and the *cis* arrangement of the ligands. Broad signals were observed in the ^1H NMR spectra, owing to the formation of a stereogenic sulfur atom after its coordination to palladium.[18e] The values of the ν(Pd−Cl) stretching vibration in the far-infrared spectrum (ca. 312 and 295 cm^{-1}) are also consistent with a *cis* arrangement of the chlorides.[19a,26] Using a stronger base, such as KO*t*-Bu, on a similar system, Wolf et al. observed the formation of a dinuclear species, in which the ligand acted as a *C*,*S*-bridge between two metal centers.[18h] The solid-state molecular structures of complexes **10** and **12** are depicted in Figures 3 and 4, respectively. They are very similar, and in each case, the complexes adopt a distorted square-planar geometry around the palladium centers. The ligands form a *C*,*S* chelate with a bite angle of 83.19(11)° and 88.99(13)° for **10** and **12**, respectively. The higher *trans* influence of the carbene ligands compared to the sulfur is illustrated by longer Pd(1)−Cl(1) bonds compared to Pd(1)−Cl(2). The six-membered palladacycle formed by the metal and the chelate ligand adopts a boat-like conformation, in which C(4) and Pd(1) are on the same side of the C1−N2(1)−C5−S1 plane. Due to the short side chain (two methylene groups) and coordination of the sulfur atom, the angles between the imidazole ring and the palladium coordination plane deviate from the electronically preferred 90°, with values of 56.8(3)° and 53.1(9)° for **10** and **12**, respectively.

(23) (a) Teo, B.-K.; Calabrese, J. C. *Inorg. Chem.* **1976**, *15*, 2474. (b) Teo, B.-K.; Calabrese, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 1256.

(24) See e.g. (for poly-NHCs): (a) Rit, A.; Pape, T.; Hahn, F. E. *J. Am. Chem. Soc.* **2010**, *132*, 4572. (b) Hahn, F. E.; Radloff, C.; Pape, T.; Hepp, A. *Chem.—Eur. J.* **2008**, *14*, 10900. (For N-): (c) Li, F.; Bai, S.; Hor, T. S. A. *Organometallics* **2008**, *27*, 672. (d) Tulloch, A. A. D.; Danopoulos, A. A.; Winston, S.; Kleinhenz, S.; Easthamb, G. *J. Chem. Soc., Dalton Trans.* **2000**, 4499. (For P-): Raynal, M.; Liu, X.; Pattacini, R.; Vallée, C.; Olivier-Bourbigou, H.; Braunstein, P. *Dalton Trans.* **2009**, 7288.

(25) (a) Clark, R. J. H.; Williams, C. S. *Inorg. Chem.* **1965**, *4*, 350. (b) Bencze, É.; Pápai, I.; Mink, J.; Goggin, P. L. *J. Organomet. Chem.* **1999**, *584*, 118.

(26) Pfeffer, M.; Braunstein, P.; Dehand, J. *Spectrochim. Acta* **1974**, *30A*, 341.

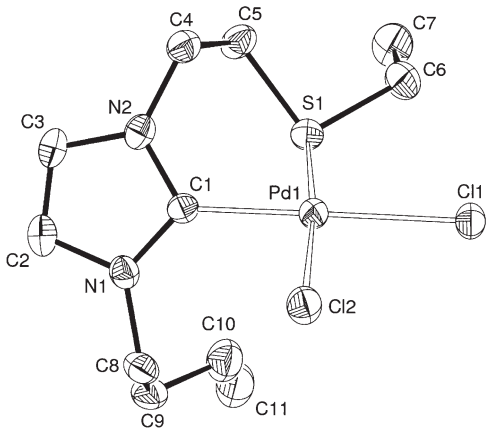


Figure 3. View of the molecular structure of **10**. Hydrogen atoms are omitted for clarity. Ellipsoids are represented at the 50% probability level. Selected bond lengths (Å) and bond angles (deg): Pd1−C1 1.989(4), Pd1−S1 2.2955(11), Pd1−Cl1 2.3631(10), Pd1−Cl2 2.3317(10), C1−N1 1.333(5), C1−N2 1.342(5), C1−Pd1−S1 83.19(11), C1−Pd1−Cl2 90.99(11), S1−Pd1−Cl1 93.30(4), N1−C1−N2 106.8(3).

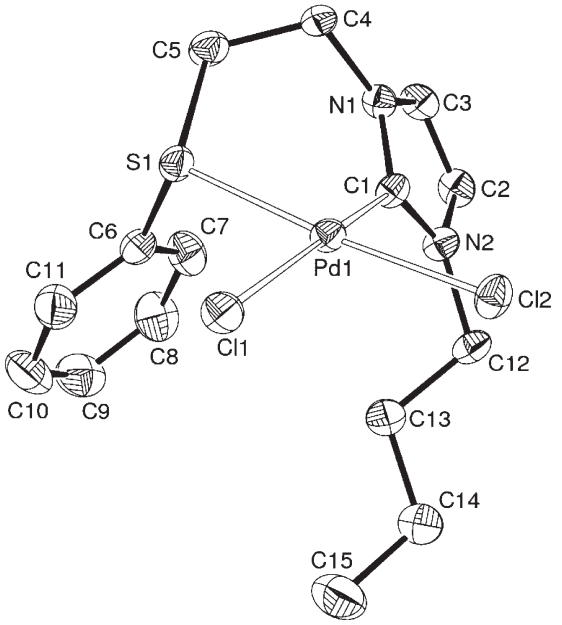


Figure 4. View of the molecular structure of **12**. Hydrogen atoms are omitted for clarity. Ellipsoids are represented at the 50% probability level. Selected bond lengths (Å) and bond angles (deg): Pd1−C1 1.978(4), Pd1−S1 2.2858(12), Pd1−Cl1 2.3709(12), Pd1−Cl2 2.3301(12), C1−N1 1.340(5), C1−N2 1.346(5), C1−Pd1−S1 88.99(13), C1−Pd1−Cl2 91.89(13), S1−Pd1−Cl1 86.55(4), N1−C1−N2 106.0(4).

By using the procedure of route B (Scheme 3, c and d), which has only limited precedents,[18h,19a] we found that the presence of a thioether moiety exerts a favorable anchimeric assistance for the selective formation of $[PdCl_2(S,C_{NHC})]$ chelate complexes without the constraints of a transmetalation reaction. Another beneficial aspect of this method compared to transmetalation is that the catalyst precursor can be formed directly *in situ* and immediately engaged in a catalytic process with no silver contamination. This has been tested with **1**·HCl to form *in situ* complex **9** in the catalytic studies described below.

Synthesis of the Bis-NHC Palladium(II) Complexes. Since NHC ligands are known to be strong donor ligands that rarely dissociate from the metal, the presence of two NHC ligands on the palladium center could lead to attractive species for catalytic applications. Two types of bis-carbene palladium complexes were synthesized in the course of this work.

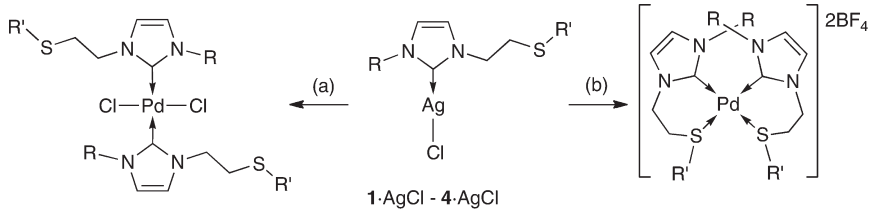
Starting from the corresponding silver complexes synthesized *in situ*, reaction with $[PdCl_2(cod)]$ in a 2:1 ratio afforded the bis-carbene palladium dichloride complexes of general formula $[PdCl_2(\mathbf{L})_2]$, **17**−**20** (Scheme 5, a). Only one isomer was formed during the reaction, and the NMR spectra of these complexes showed only one set of signals for the ligands. The sharp ^{1}H NMR signals are consistent with dangling lateral side chains bonded to the nitrogen atoms. At this stage, it is reasonable to suggest that the *trans* isomer is formed, and the value of the ν(Pd−Cl) stretching vibration around 340 cm^{-1} is in accordance with this hypothesis.[26] The *trans-anti* arrangement was confirmed by the solid-state X-ray structures of **17**[18e] and **18** (Figure 5). The palladium atom occupies a center of symmetry for the molecule, and the square-planar coordination geometry around the palladium center is only slightly distorted (C1−Pd1−Cl1 90.3(1)°).

A second type of bis-NHC palladium complexes was synthesized, starting from the silver complexes **1**·AgCl−**4**·AgCl. Reaction of 0.5 equiv of $[Pd(NCMe)_4][BF_4]_2$ with the corresponding silver complex generated *in situ*, at room temperature in dichloromethane, afforded the dicationic, bis-chelated palladium(II) complexes **21**−**24**, of general formula $[Pd(S,C_{NHC})_2][BF_4]_2$. Their formation results from the easy displacement of the palladium-bound acetonitrile ligands, which was confirmed by ^{1}H NMR spectroscopy. Only a few examples of bis-chelated dicationic Pd complexes, with donor-functionalized NHC ligands, have been described, and they showed interesting catalytic activities in coupling reactions.[13a,27] Bis-chelated dicationic $[Pd(N,C_{NHC})_2]X_2$ with *N* representing a picoline donor moiety were recently reported and have been studied in Heck-type coupling reactions.[13a,g] To the best of our knowledge, no example with thioether side chains was reported. Such complexes could offer advantages for catalytic applications: they bear two strong ligands known to be efficient in homogeneous catalysis and have two coordination sites readily accessible by displacement of the soft sulfur ligands. These properties could lead to catalysts active for Suzuki−Miyaura couplings under very mild, room-temperature conditions.[28] Like in the case of the monochelate palladium dichloride complexes, the sulfur atom becomes a stereogenic center upon coordination to the metal center, and this gives rise to a broadening of the ^{1}H NMR resonances. This is in accordance with the bis-chelation of the ligands in the dicationic complexes, whereas sharp signals were observed for the dichloro-bis-NHC complexes. The broadening is due to a more rigid structure of the side chain, in contrast to the situation in the dichloro complexes. The carbenic carbons of **21**−**24** resonate, in the $^{13}C\{^1H\}$ NMR, between 155.1 and 157.8 ppm, strongly upfield shifted compared to the neutral *trans* complexes, e.g., 170.1 ppm for **20**, and to reported $[Pd(N,C_{NHC})_2][BF_4]_2$ complexes

(27) (a) Zhang, X.; Xia, Q.; Chen, W. *Dalton Trans.* **2009**, 7045. (b) Zhang, X.; Xi, Z.; Liu, A.; Chen, W. *Organometallics* **2008**, *27*, 4401. (c) Ye, J.; Chen, W.; Wang, D. *Dalton Trans.* **2008**, 4015. (d) Chiu, P. L.; Lai, C.-L.; Chang, C.-F.; Hu, C.-H.; Lee, H. M. *Organometallics* **2005**, *24*, 6169. (e) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741.

(28) Nishikata, T.; Abela, A. R.; Huang, S.; Lipshutz, B. H. *J. Am. Chem. Soc.* **2010**, *132*, 4978, and references therein.

Scheme 5. Synthetic Pathways for the Synthesis of Bis-NHC Palladium(II) Complexes[a]



17 R = Me; R' = Et
18 R = *n*-Bu; R' = Et
19 R = Me; R' = Ph
20 R = *n*-Bu; R' = Ph

1 R = Me; R' = Et
2 R = *n*-Bu; R' = Et
3 R = Me; R' = Ph
4 R = *n*-Bu; R' = Ph

21 R = Me; R' = Et
22 R = *n*-Bu; R' = Et
23 R = Me; R' = Ph
24 R = *n*-Bu; R' = Ph

[a] (a) 1/2 equiv $[PdCl_2(cod)]$, CH_2Cl_2, RT ; (b) 1/2 equiv $[Pd(NCMe)_4][BF_4]_2$, CH_2Cl_2, RT.

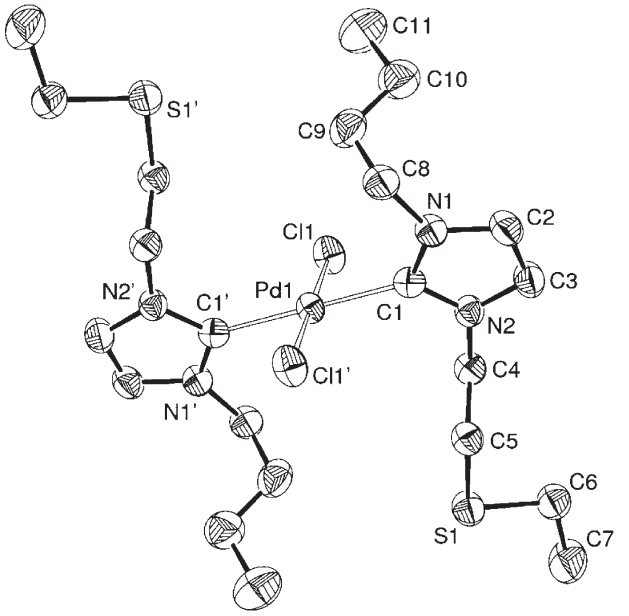


Figure 5. View of the molecular structure of **18**. Only one of the two analogous crystallographically independent molecules is depicted. Hydrogen atoms are omitted for clarity. Ellipsoids are represented at the 50% probability level. Selected bond lengths (Å) and bond angles (deg): Pd1−C1 2.025(4), Pd1−Cl1 2.3094(10), C1−N1 1.351(5), C1−N2 1.349(5), C1−Pd1−Cl1 90.29(11), N1−C1−N2 105.3(3).

(N-donor from a picoline moiety in a *cis* arrangement) between 167.3 and 166.1 ppm,[13a,g] but more downfield than a $[Pd(N,C_{NHC})_2][PF_6]_2$ complex (150.9 ppm).[27d] This very large upfield shift results from the *cis* arrangement of the carbene donors, the coordination of the thioether function, and the formally dicationic charge on the Pd center. The latter will increase the donation from the carbenic carbon, which is illustrated by the value of their chemical shift. We could thus show that selective formation of *trans*-$[PdCl_2(C_{NHC})_2]$ and *cis*-$[Pd(S,C_{NHC})_2][BF_4]_2$ complexes is possible starting from readily accessible Ag(NHC) complexes.

Catalytic Studies. The palladium complexes **9**−**24** were evaluated in Suzuki−Miyaura cross-coupling reactions. The complexes were first tested using the procedure described in Scheme 6, and then for the most interesting complexes, the conditions were varied. The results obtained with the mono-NHC complexes **9**−**16** are reported in Table 1.

The choice of DMSO as a solvent resulted from the low solubility of these complexes in dioxane, which is the common solvent for this reaction. The conversions to 4-methyl-biphenyl observed with the chelate complexes **9**−**12** are nearly quantitative. The best yields, 94% and 91%, were obtained for the complexes bearing an N-*n*-Bu substituent, **10** and **12**, respectively. The presence of this side chain probably induces a higher solubility of the precursors. The conversions observed with the zwitterionic compounds **13**−**16** were lower than those obtained with the corresponding chelate species.

Scheme 6. Typical Procedure for the Catalytic Reactions

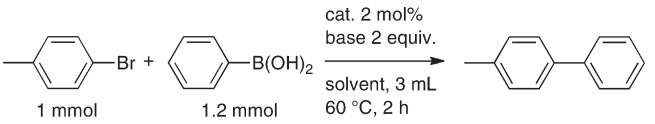


Table 1. Catalytic Activities for Mono-NHC Palladium Complexes[a]

complex	yield (%)	complex	yield (%)
9	88	**13**	62,[a] 86[b]
10	94	**14**	71,[a] 95[b]
11	86	**15**	51,[a] 87[b]
12	91	**16**	47,[a] 91[b]

[a] Yields determined by GC. Reaction conditions: cat. 2 mol %, base Cs_2CO_3, solvent DMSO, temp 60 °C, reaction time 2 h. [b] Reaction time 5 h.

The reaction mixtures did not turn dark with formation of potentially active Pd(0) species, in contrast to the case of the NHC complexes **9**−**12**. Runs performed with **13**−**16** for 5 h reaction time led to similar yields to those in the case of the chelated precatalysts (±2%). Assuming that the zwitterionic compounds **13**−**16** are not the direct catalyst precursors, but are first transformed during the induction period to the corresponding neutral chelate species **9**−**12**, a catalytic reaction starting from complex **13** was run for 6 h and a plot of the yield as a function of time is shown in Figure 6.

During the first 2 h, almost no conversion was observed, this time being necessary for the formation of the carbene complex **9** by deprotonation of **13** by the slight excess of base present in the reaction mixture. During the next 3 h, the conversion was similar to that observed when starting from complex **9** (Figure 6). This experiment indicates the stepwise formation of the precatalyst in the reactor by reaction of the imidazolium salt, the palladium precursor, and the base used for the catalytic reaction. It could be interesting to extend this procedure to other metal complexes such as Ni(II) or Rh(I) and to donor functions like amines or phosphines, which are involved in diverse catalytic reactions. With the

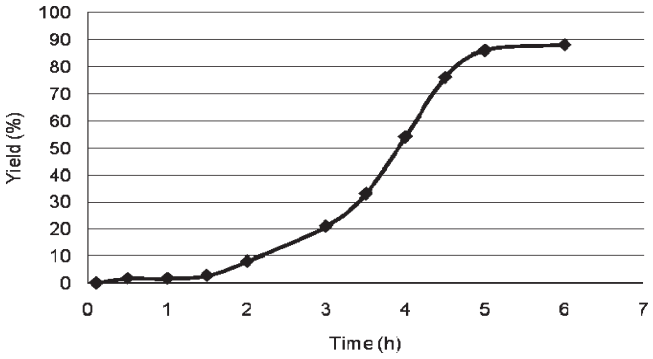


Figure 6. Evolution of the conversion to 4-methyl-biphenyl as a function of time in the Suzuki−Miyaura cross-coupling reaction starting from zwitterionic complex **13**.

Table 2. Solvent and Base Effects on the Catalysis Reaction with Complex 10[a]

solvent	yield[b] (%)	base	yield[c] (%)
dioxane	80	NaOAc	36
DMSO	94	$NaCO_3$	74
DMF	57	K_2CO_3	70
toluene	71	NEt_3	29
water	0	Cs_2CO_3	91

[a] Yields determined by GC. Reaction conditions: cat. 2 mol %, base, solvent, temp 60 °C, time 2 h. [b] Base Cs_2CO_3. [c] Solvent DMSO.

Table 3. Catalytic Activities for Bis-NHC Palladium Complexes[a]

complex	yield (%)	complex	yield (%)
17	74	**21**	90
18	68	**22**	98
19	72	**23**	91
20	79	**24**	96

[a] Yields determined by GC. Reaction conditions: cat. 2 mol %, base Cs_2CO_3, solvent DMSO, temp 60 °C, reaction time 2 h.

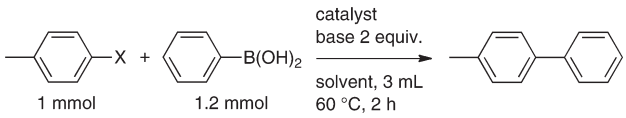
most efficient catalyst precursor, complex **10**, different solvents and bases were used to optimize the reaction conditions (Table 2). As expected, the highly polar solvent DMSO was the best for these complexes (94%), but we also observed a good activity with toluene as solvent (71%). DMF, another polar solvent, was also tested, but no better activity than in the case of DMSO was observed. Four inorganic bases were tested with this complex, and carbonates were the most efficient, Cs_2CO_3 being the best (91%). The organic base NEt_3 gave rise to less than 30% conversion (Table 2).

The bis-NHC palladium complexes **17**−**24** were also evaluated in Suzuki−Miyaura cross-coupling reactions, and the results obtained are reported in Table 3. The catalytic tests were performed under the conditions optimized for the mono-NHC palladium complexes (see above). The dichloride compounds led to relatively good yields, between 68% (**18**) and 79% (**20**). Finally, with the dicationic, bis-chelated species **21**−**24**, the best activities of all the palladium complexes synthesized in this work were observed, especially with complex **22**, which gave 98% conversion.

In view of these results, further experiments were performed with the best catalysts. These were tested first with a lower catalyst loading and then with *p*-chlorotoluene as substrate. The results of these catalytic runs are reported in Table 4.

With complexes **10** and **22**, a decrease of the conversion was observed when 1 mol % precatalyst was used instead of 2 mol %, as in the previous experiments; however, the conversion was not divided by two. It is more difficult to achieve the cross-coupling reaction with chlorinated than with brominated substrates,[29] which explains the drop of the conversion from 94% (**10**) and 98% (**22**) to 30% and 38% for **10** and **22**, respectively.

Table 4. Catalytic Activities of Complexes 10 and 22 under Modified Reaction Conditions[a]



complex	yield[b] (%)	complex	yield[c] (%)
10	54	**10**	30
22	58	**22**	38

[a] Yields determined by GC. Reaction conditions: base Cs_2CO_3, solvent DMSO, temp 60 °C, reaction time 2 h. [b] Catalyst 1 mol %, X = Br. [c] Catalyst 2 mol %, X = Cl.

Conclusion

The scope of a procedure recently described for the synthesis of new functionalized N-heterocyclic carbene precursors bearing as side arms a bulky aromatic group and a thioether function able to coordinate to a metal center has been extended and could gain wider applicability.[18e,19a] Thus, linking an imidazolium cation to a metal center via its functional side chain tends to favor its subsequent deprotonation and formation of the carbene−metal bond. Four different types of palladium(II) complexes bearing thioether-NHC ligands were obtained, and the ligand was acting as a S,C_{NHC} chelate in complexes **9**−**12** and **21**−**24**. However, an unprecedented planar Ag_4I_4 cluster has been structurally characterized in which the S,C_{NHC} ligand bridges two Ag centers with different coordination geometries. Among the Pd(II) complexes that were evaluated in Suzuki−Miyaura cross-coupling reactions, a higher catalytic activity was observed for those in which the sulfur atom is coordinated to the metal center. It will be interesting to see whether similar observations apply to other catalytic reactions.

Experimental Section

General Procedures. All operations were carried out using standard Schlenk techniques under inert atmosphere. Solvents were purified and dried under nitrogen by conventional methods. d_6-DMSO was degassed and stored over 4 Å molecular sieves. CD_2Cl_2, $CDCl_3$, and CD_3CN were dried over 4 Å molecular sieves, degassed by freeze−pump−thaw cycles, and stored under argon. NMR spectra were recorded at room temperature on a Bruker AVANCE 300 spectrometer (^1H, 300 MHz; ^{13}C, 75.47 MHz; ^{31}P, 121.49 MHz; and ^{19}F, 282.38 MHz) and referenced using the residual proton solvent (^1H) or solvent (^{13}C) resonance. Assignments are based on ^1H, ^1H−COSY, ^1H, ^{13}C-HMQC, and ^1H, ^{13}C-HMBC experiments. Chemical shifts (δ) are given in ppm. IR spectra were recorded in the region 4000−100 cm^{-1} on a Nicolet 6700 FT-IR spectrometer (ATR mode, SMART ORBIT accessory, Diamond crystal). Elemental analyses were performed by the "Service de Microanalyses", Université de Strasbourg, and by the "Service Central d'Analyse", USR-59/CNRS, Solaize. Electrospray mass spectra (ESI-MS) were recorded on a microTOF (Bruker Daltonics, Bremen, Germany) instrument using nitrogen

(29) (a) Diebolt, O.; Braunstein, P.; Nolan, S. P.; Cazin, C. S. J. *Chem. Commun.* **2008**, 3190. (b) Bedford, R. B.; Cazin, C. S. J.; Holder, D. *Coord. Chem. Rev.* **2004**, *248*, 2283. (c) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176. (d) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047.

as drying agent and nebulizing gas, and Maldi-TOF analyses were carried out on a Bruker AutiflexII TOF/TOF (Bruker Daltonics, Bremen, Germany), using dithranol (1,8,9-trihydroxyanthracene) as a matrix. Gas chromatographic analyses were performed on a Thermoquest GC8000 Top series gas chromatograph using a HP Pona column (50 m, 0.2 mm diameter, 0.5 μm film thickness). The imidazolium salts **1**·HCl to **4**·HCl[18e] and the complexes [$PdCl_2$(cod)],[30] [$Pd(NCMe)_4$][BF_4]$_2$,[31] **1**·AgCl−**4**·AgCl,[18e] **9**,[18e] and **17**[18e] were prepared according to literature methods. All other reagents were used as received from commercial suppliers.

Abbreviations: Mes = 2,4,6-trimethylphenyl; Diip = 2,6-diisopropylphenyl; KHMDS = potassium hexamethyldisilazane.

Synthesis of *N*-(R)-*N*′-Ethyl-(R′)-sulfide Imidazolium Iodides 5·HI−8·HI. These compounds are known to be very hygroscopic, and the elemental analyses always afforded carbon and nitrogen percentages lower than calculated values.

5·HI: R = 2,4,6-trimethylphenyl; R′ = ethyl. Pure *N*-(2,4,6-trimethylphenyl)imidazole (2.00 g, 10.74 mmol), 2-chloroethyl ethylsulfide (1.25 mL, 1.34 g, 10.74 mmol), and sodium iodide (3.22 g, 21.48 mmol) were placed in a Schlenk tube equipped with a magnetic stirrer, and toluene was added. The mixture was refluxed for 2 h and then allowed to cool to room temperature. During heating, the colorless mixture turned light brown. After cooling, the mixture was filtered to eliminate the excess of salts formed and/or remaining. The volatiles were evaporated under reduced pressure, and the brown oil was washed with dry diethyl ether (2 × 40 mL) and dried under vacuum. The residue was purified by precipitation from a saturated MeOH solution in cold Et_2O. The product was isolated as a yellow oil. Yield: 84%. Anal. Calcd for $C_{16}H_{23}IN_2S$ (402.34): C, 47.76; H, 5.76; N, 6.96. Found: C, 45.51; H, 6.13; N, 5.76. FTIR: ν_{max}(oil)/cm^{-1}: 3118sh, 3057br, 2968br, 2920br, 2866sh, 1606w, 1561m, 1545s, 1484m, 1446s, 1376w, 1329w, 1263w, 1199vs, 1157s, 1104w, 1067s, 1034m, 968w, 934w, 854s, 750m, 730sh, 698w, 666s. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.24 (3H, t, ^3J = 7.2 Hz, SCH_2CH_3), 2.10 (6H, s, 2 CH_3 *ortho*-Mes), 2.34 (3H, s, CH_3 *para*-Mes), 2.68 (2H, q, ^3J = 7.2 Hz, SCH_2CH_3), 3.13 (2H, t, ^3J = 6.0 Hz, NCH_2CH_2S), 4.95 (2H, t, ^3J = 6.0 Hz, NCH_2CH_2S), 7.01 (2H, s, 2*H* *meta*-Mes), 7.18 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, CH=C*H*NCH$_2$), 7.98 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, MesNC*H*=CH), 9.78 (1H, t, ^4J = 1.5 Hz, NCHN). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz) δ: 14.74 (SCH_2CH_3), 17.89 (2 CH_3 *ortho*-Mes), 21.16 (CH_3 *para*-Mes), 26.14 (SCH_2CH_3), 32.29 (NCH_2CH_2S), 49.71 (NCH_2CH_2S), 123.00, 123.65 (CH=CH), 129.92 (2 *C*H *meta*-Mes), 130.48 (*C ipso*-Mes), 134.40 (2 *C ortho*-Mes), 137.69 (NCN), 141.51 (*C para*-Mes). MS (ESI): m/z 275.2 [M − I]$^+$.

6·HI: R = 2,6-diisopropylphenyl; R′ = ethyl. The same procedure was used with *N*-(2,6-diisopropylphenyl)imidazole (5.07 g, 27.20 mmol), 2-chloroethyl ethylsulfide (4.00 mL, 4.70 g, 27.20 mmol), and sodium iodide (8.15 g, 54.39 mmol). The product was isolated as a yellow oil. Yield: 81%. Anal. Calcd for $C_{19}H_{29}IN_2S$ (444.42): C, 51.35; H, 6.58; N, 6.30. Found: C, 48.96; H, 6.62; N, 5.30. FTIR: ν_{max}(oil)/cm^{-1}: 3152br, 3071br, 2964br, 2929br, 2871br, 1592w, 1564m, 1547m, 1458m, 1414sh, 1387w, 1367m, 1315w, 1264w, 1245sh, 1190m, 1130sh, 1105m, 1071m, 1060m, 959w, 938w, 874sh, 829vs, 759s, 739s, 693m, 670s. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.82−0.99 (15H, 2d, ^3J = 6.9 Hz, 2 CH(CH_3)$_2$, and t, ^3J = 7.2 Hz, SCH_2CH_3,), 2.10 (2H, sept, ^3J = 6.6 Hz, 2 C*H*(CH$_3$)$_2$), 2.44 (2H, q, ^3J = 7.4 Hz, SCH_2CH_3), 2.89 (2H, t, ^3J = 6.0 Hz, NCH_2CH_2S), 4.72 (2H, t, ^3J = 6.0 Hz, NCH_2CH_2S), 7.02 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, CH=C*H*NCH$_2$), 7.16 (2H, d, ^3J = 8.1 Hz, 2*H* *meta*-Diip), 7.27 (1H, t, ^3J = 8.1 Hz, *H para*-Diip), 8.28 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, DiipNC*H*=CH), 9.76 (1H, t, ^4J = 1.5 Hz, NCHN). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz) δ: 14.41 (SCH_2CH_3), 24.00, 24.42 (2 CHCH_3), 25.60 (SCH_2CH_3), 28.29 (2 *C*HCH_3), 32.30 (NCH_2CH_2S), 48.56 (NCH_2CH_2S), 123.58, 124.02 (CH=CH), 124.42 (*C*H *meta*-Diip), 128.67 (*C ipso*-Diip), 131.68 (*C*H *para*-Diip), 137.75 (NCN), 145.28 (*C ortho*-Diip). MS (ESI): m/z 317.2 [M − I]$^+$.

7·HI: R = 2,4,6-trimethylphenyl; R′ = phenyl. The same procedure was used with *N*-(2,4,6-trimethylphenyl)imidazole (5.07 g, 27.20 mmol), 2-chloroethyl phenylsulfide (4.00 mL, 4.70 g, 27.20 mmol), and sodium iodide (8.15 g, 54.39 mmol). The product was isolated as a yellow solid. Yield: 85%. Anal. Calcd for $C_{20}H_{23}IN_2S$ (450.38): C, 53.34; H, 5.15; N, 6.22. Found: C, 51.73; H, 5.27; N, 4.82. FTIR: ν_{max}(solid)/cm^{-1}: 3145br, 3096w, 3050br, 2947w, 1627w, 1604w, 1581w, 1561m, 1547s, 1479m, 1446s, 1436s, 1380w, 1364w, 1346w, 1324w, 1280w, 1247w, 1200vs, 1154s, 1109w, 1087w, 1067s, 1035m, 1023m, 967w, 935w, 865s, 821m, 782m, 743vs, 703m, 692vs, 663vs ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.05 (6H, s, 2 CH_3 *ortho*-Mes), 2.32 (3H, s, CH_3 *para*-Mes), 3.62 (2H, t, ^3J = 6.0 Hz, NCH_2CH_2S), 4.90 (2H, t, ^3J = 6.0 Hz, NCH_2CH_2S), 6.98 (2H, s, 2*H* *meta*-Mes), 7.17 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, CH=C*H*NCH$_2$), 7.20−7.37 (5H, m, H aromatics), 8.01 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, MesNC*H*=CH), 9.69 (1H, t, ^4J = 1.5 Hz, NCHN). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz) δ: 17.88 (2 CH_3 *ortho*-Mes), 21.15 (CH_3 *para*-Mes), 34.85 (NCH_2CH_2S), 49.25 (NCH_2CH_2S), 122.98, 123.34 (CH=CH), 127.32 (*C*H *para*-phenyl), 129.64 (2 *C*H *meta*-phenyl), 129.90 (2 *C*H *meta*-Mes), 130.01 (2 *C*H *ortho*-phenyl), 130.44 (*C ipso*-Mes), 133.28 (*C ipso*-phenyl), 134.32 (2 *C ortho*-Mes), 137.26 (NCN), 141.50 (*C para*-Mes). MS (ESI): m/z 323.2 [M − I]$^+$.

8·HI: R = 2,6-diisopropylphenyl; R′ = phenyl. The same procedure was used with *N*-(2,6-diisopropylphenyl)imidazole (5.07 g, 27.20 mmol), 2-chloroethyl phenylsulfide (4.00 mL, 4.70 g, 27.20 mmol), and sodium iodide (8.15 g, 54.39 mmol). The product was isolated as a yellow solid. Yield: 92%. Anal. Calcd for $C_{23}H_{29}IN_2S$ (492.46): C, 56.10; H, 5.94; N, 5.69. Found: C, 55.01; H, 5.80; N, 4.46. FTIR: ν_{max}(solid)/cm^{-1}: 3148br, 3053br, 2967br, 2929br, 2871br, 1584w, 1562w, 1546w, 1459m, 1440w, 1420w, 1388w, 1367w, 1354sh, 1313w, 1264s, 1187m, 1103w, 1088sh, 1070w, 1059w, 1025w, 895w, 844s, 806m, 730vs, 700vs, 671s. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.19 (12H, 2 d, ^3J = 6.9 Hz, 2 CH(CH_3)$_2$), 2.34 (2H, sept, ^3J = 6.9 Hz, 2 C*H*(CH$_3$)$_2$), 3.62 (2H, t, ^3J = 5.7 Hz, NCH_2CH_2S), 4.90 (2H, t, ^3J = 5.7 Hz, NCH_2CH_2S), 7.21 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, CH=C*H*NCH$_2$), 7.25−7.33 (7H,m, 5*H* phenyl and 2*H* *meta*-Diip), 7.55 (1H, t, ^3J = 7.8 Hz, *H para*-Diip), 8.03 (1H, pseudo t, ^3J = ^4J = 1.7 Hz, DiipNC*H*=CH), 9.26 (1H, t, ^4J = 1.5 Hz, NCHN). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz) δ: 24.41 (2 CHCH_3), 28.69 (2 *C*HCH_3), 34.96 (NCH_2CH_2S), 49.24 (NCH_2CH_2S), 124.17, 124.21 (CH=CH), 124.82 (2 *C*H *meta*-Diip), 127.46 (*C*H *para*-phenyl), 129.72 (2 *C*H *meta*-phenyl), 129.81 (*C ipso*-Diip), 129.91 (2 *C*H *ortho*-phenyl), 132.16 (*C*H *para*-Diip), 133.00 (*C ipso*-phenyl), 137.19 (NCN), 145.52 (*C ortho*-Diip). MS (ESI): m/z 365.2 [M − I]$^+$.

General Procedure for the Anion Exchange.

6·HPF_6: R = 2,6-diisopropylphenyl ; R′ = ethyl. The imidazolium iodide **6**·HI (0.200 g, 0.45 mmol) and solid KPF_6 (0.414 g, 2.25 mmol) were mixed in CH_2Cl_2 and stirred for 2 days at room temperature. Then the suspension was filtered through a Celite pad, and the solvent was evaporated under reduced pressure to give a yellow solid. Yield: 97%. Anal. Calcd for $C_{19}H_{29}F_6N_2PS$ (462.48): C, 49.34; H, 6.32; N, 6.06. Found: C, 48.96; H, 6.47; N, 6.24. FTIR: ν_{max}(solid)/cm^{-1}: 3151br, 2966br, 2930br, 2872br, 2360br, 1626br, 1564m, 1548m, 1459m, 1388w, 1367w, 1315w, 1261w, 1216w, 1190m, 1104w, 1071w, 1060w, 911s, 837vs, 806sh, 757sh, 729vs, 669s. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.17 (12H, 2 d, ^3J = 6.9 Hz, 2 CH(CH_3)$_2$), 1.22 (3H, t, ^3J = 7.2 Hz, SCH_2CH_3), 2.35 (2H, sept, ^3J = 6.9 Hz, 2 C*H*(CH$_3$)$_2$), 2.62 (2H, q, ^3J = 7.2 Hz, SCH_2CH_3), 3.06 (2H, t, ^3J = 6.0 Hz, NCH_2CH_2S), 4.74 (2H, t, ^3J = 6.0 Hz, NCH_2CH_2S), 7.21 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, CH=C*H*NCH$_2$), 7.30 (2H, d, ^3J = 8.1 Hz, 2*H* *meta*-Diip), 7.53 (1H, t, ^3J = 8.1 Hz, *H para*-Diip), 7.91 (1H, pseudo t, ^3J = ^4J = 1.8 Hz, DiipNC*H*=CH), 9.04 (1H, t, ^4J = 1.5 Hz, NCHN). ^{13}C{^{1}H}

(30) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1972**, *13*, 47.
(31) Wayland, B. B.; Schrammz, R. F. *Inorg. Chem.* **1969**, *8*, 971.

NMR ($CDCl_3$, 75.5 MHz) δ: 14.55 (SCH_2CH_3), 24.22, 24.29 (2 $CHCH_3$), 25.59 (SCH_2CH_3), 28.56 (2 $CHCH_3$), 32.18 (NCH_2CH_2S), 49.23 (NCH_2CH_2S), 123.43, 124.53 (CH=CH), 124.69 (*CH meta*-Diip), 129.89 (*C ipso*-Diip), 132.00 (*CH para*-Diip), 137.39 (NCN), 145.59 (*C ortho*-Diip). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz) δ: −142.9 (sept., $^1J_{P,F}$ = 711 Hz, PF_6). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 282.4 MHz) δ: −72.5 (d, $^1J_{P,F}$ = 711 Hz, PF_6). MS (ESI): m/z 317.2 $[M - PF_6]^+$.

8·HPF$_6$: R = 2,6-diisopropylphenyl; R′ = phenyl. The same procedure was used with **8·HI** (0.200 g, 0.41 mmol) and solid KPF_6 (0.374 g, 2.03 mmol). The product was isolated as a yellow solid. Yield: 98%. Anal. Calcd for $C_{23}H_{29}F_6N_2PS$ (510.17): C, 54.11; H, 5.73; N, 5.49. Found: C, 54.34; H, 5.40; N, 5.09. FTIR: ν_{max}(solid)/cm^{-1}: 3155br, 3103w, 2968br, 2929w, 2872br, 1634br, 1565w, 1553m, 1474m, 1455m, 1442w, 1408w, 1389w, 1366w, 1350w, 1306w, 1288w, 1278w, 1265w, 1245w, 1217w, 1191s, 1153w, 1106w, 1089w, 1073w, 1059w, 1037w, 1024w, 1005w, 961w, 940w, 927w, 915w, 875s, 841vs, 820vs, 758vs, 698s, 671v, 652m. ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.16 (12H, 2 d, ^3J = 6.9 Hz, 2 $CH(CH_3)_2$), 2.31 (2H, sept, ^3J = 6.8 Hz, 2 $CH(CH_3)_2$), 3.50 (2H, t, ^3J = 5.9 Hz, NCH_2CH_2S), 4.66 (2H, t, ^3J = 5.8 Hz, NCH_2CH_2S), 7.22−7.33 (8H,m, CH=C*H*NCH$_2$, 5*H* phenyl and 2*H meta*-Diip), 7.54 (1H, t, ^3J = 7.8 Hz, *H para*-Diip), 7.79 (1H, pseudo t, ^3J = ^4J = 1.5 Hz, DiipNC*H*=CH), 8.68 (1H, br s, NCHN). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) δ: 24.10, 24.36 (2 $CHCH_3$), 28.59 (2 $CHCH_3$), 34.56 (NCH_2CH_2S), 49.09 (NCH_2CH_2S), 123.88 (*C*H=CH), 124.73 (br, 2 *CH meta*-Diip and CH=*CH*), 127.42 (*CH para*-phenyl), 129.68 (2 *CH meta*-phenyl), 129.84 (*C ipso*-Diip), 129.93 (2 *CH ortho*-phenyl), 132.07 (*CH para*-Diip), 133.03 (*C ipso*-phenyl), 136.87 (NCN), 145.57 (*C ortho*-Diip). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz) δ: −143.1 (sept., $^1J_{P,F}$ = 711 Hz, PF_6). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 282.4 MHz) δ: −72.4 (d, $^1J_{P,F}$ = 711 Hz, PF_6). MS (ESI): m/z 365.2 $[M - PF_6]^+$.

Synthesis of the Thiones 1·S−4·S.

1·S: R = methyl; R′ = ethyl. Solid KHMDS (0.289 g, 1.45 mmol) was added to a stirred suspension of **1·HCl** (0.300 g, 1.45 mmol) and S_8 (0.186 g, 0.73 mmol) in THF at room temperature. After 2 h, the reaction mixture was filtered through a Celite pad and the THF evaporated under reduced pressure. The residue was washed with pentane (2 × 20 mL) and dried under vacuum. The product was obtained as an orange solid. Yield: 72%. Anal. Calcd for $C_8H_{14}N_2S_2$ (202.34): C, 47.49; H, 6.97; N, 13.84. Found: C, 47.09; H, 7.26; N, 13.73. FTIR: ν_{max}(solid)/cm^{-1}: 3159br, 3125br, 3093br, 2956br, 2926br, 2869br, 1666w, 1582w, 1567w, 1457s, 1438s, 1400vs, 1358m, 1332m, 1265w, 1227s (tentatively assigned to the C=S stretching vibration), 1205sh, 1182s, 1133w, 1086w, 1061w, 1023w, 971w, 936w, 872w, 797sh, 739m, 708s, 691sh, 669vs ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.26 (3H, t, ^3J = 7.5 Hz, SCH_2CH_3), 2.57 (2H, q, ^3J = 7.5 Hz, SCH_2CH_3), 2.92 (2H, t, ^3J = 6.9 Hz, NCH_2CH_2S), 3.60 (3H, s, NCH_3), 4.20 (2H, t, ^3J = 6.9 Hz, NCH_2CH_2S), 6.67 and 6.75 (2H, AB spin system, ^3J = 2.4 Hz, CH=CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) δ: 14.85 (SCH_2CH_3), 26.19 (SCH_2CH_3), 30.06 (NCH_2CH_2S), 35.10 (NCH_3), 48.01 (NCH_2CH_2S), 117.30, 117.49 (CH=CH), 162.09 (NCN). MS (ESI): m/z 225.1 $[M + OLi]^+$.

2·S: R = *n*-butyl; R′ = ethyl. The same procedure was used with KHMDS (0.241 g, 1.21 mmol), **2·HCl** (0.300 g, 1.21 mmol), and S_8 (0.155 g, 0.60 mmol). The product was isolated as an orange solid. Yield: 69%. Anal. Calcd for $C_{11}H_{20}N_2S_2$ (244.42): C, 54.05; H, 8.25; N, 11.46. Found: C, 53.68; H, 8.41; N, 11.20. FTIR: ν_{max}(solid)/cm^{-1}: 3127br, 3094br, 2956br, 2928br, 2869br, 1734w, 1671m, 1582w, 1568w, 1520w, 1480sh, 1455sh, 1438s, 1411vs, 1358m, 1268br, 1229s (tentatively assigned to the C=S stretching vibration), 1207m, 1173m, 1117w, 1087w, 1067w, 1047w, 1024w, 876w, 740s, 712m, 691m, 672 m. ^1H NMR ($CDCl_3$, 300 MHz) δ: 0.93 (3H, t, ^3J = 7.5 Hz, CH_3 butyl), 1.24 (3H, t, ^3J = 7.5 Hz, SCH_2CH_3), 1.36 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.73 (2H, m, $NCH_2CH_2CH_2CH_3$), 2.54 (2H, q, ^3J = 7.5 Hz, SCH_2CH_3), 2.91 (2H, t, ^3J = 6.9 Hz, NCH_2CH_2S), 4.01 (2H, t, ^3J = 7.5 Hz, $NCH_2CH_2CH_2CH_3$), 4.20 (2H, t, ^3J = 7.2 Hz, NCH_2CH_2S), 6.66 and 6.75 (2H, AB spin system, ^3J = 2.4 Hz, CH=CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) δ: 13.70 (CH_3 butyl), 14.86 (SCH_2CH_3), 19.80 ($NCH_2CH_2CH_2CH_3$), 26.19 (SCH_2CH_3), 30.02 (NCH_2CH_2S), 30.96 ($NCH_2CH_2CH_2CH_3$), 47.63 ($NCH_2CH_2CH_2CH_3$), 47.92 (NCH_2CH_2S), 116.44, 117.44 (CH=CH), 161.56 (NCN). MS (ESI): m/z 251.1 $[M + Li]^+$.

3·S: R = methyl; R′ = phenyl. The same procedure was used with KHMDS (0.235 g, 1.18 mmol), **3·HCl** (0.300 g, 1.18 mmol), and S_8 (0.151 g, 0.59 mmol). The product was isolated as an orange solid. Yield: 78%. Anal. Calcd for $C_{12}H_{14}N_2S_2$ (250.38): C, 57.56; H, 5.64; N, 11.19. Found: C, 57.22; H, 5.87; N, 10.71. FTIR: ν_{max}(solid)/cm^{-1}: 3307br, 3162br, 2963br, 2924br, 2869br, 2178m, 1732w, 1625w, 1534m, 1439m, 1401s, 1333w, 1225m (tentatively assigned to the C=S stretching vibration), 1186w, 1111vs, 1048w, 1017vs, 874w, 713w, 670sh, 654m. ^1H NMR ($CDCl_3$, 300 MHz) δ: 3.38 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 3.57 (3H, s, NCH_3), 4.22 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 6.59 and 6.65 (2H, AB spin system, ^3J = 2.4 Hz, CH=CH), 7.19−7.40 (5H, m, H arom). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) δ: 31.63 (NCH_2CH_2S), 35.06 (NCH_3), 47.53 (NCH_2CH_2S), 117.51, 117.72 (CH=CH), 126.40 (*C para*-phenyl), 129.10 (*C meta*-phenyl), 129.21 (*C ortho*-phenyl), 134.69 (*C ipso*-phenyl), 161.95 (NCN). MS (ESI): m/z 290.1 $[M + K]^+$.

4·S: R = *n*-butyl; R′ = phenyl. The same procedure was used with KHMDS (0.202 g, 1.01 mmol), **4·HCl** (0.300 g, 1.01 mmol), and S_8 (0.130 g, 0.51 mmol). The product was isolated as an orange solid. Yield: 80%. Anal. Calcd for $C_{15}H_{20}N_2S_2$ (292.46): C, 61.60; H, 6.89; N, 9.58. Found: C, 61.36; H, 6.42; N, 10.01. FTIR: ν_{max}(solid)/cm^{-1}: 3133br, 3053br, 2957br, 2930br, 2871br, 1667w, 1582w, 1517w, 1480sh, 1439m, 1412s, 1380w, 1358w, 1327w, 1264w, 1230m (tentatively assigned to the C=S stretching vibration), 1114m, 1087w, 1021m, 942w, 876w, 732vs, 690s, 674m. ^1H NMR ($CDCl_3$, 300 MHz) δ: 0.94 (3H, t, ^3J = 7.5 Hz, CH_3 butyl), 1.35 (2H, m, CH_2CH_3), 1.71 (2H, m, $CH_2CH_2CH_3$), 3.37 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 3.98 (2H, t, ^3J = 7.5 Hz, $NCH_2CH_2CH_2$), 4.22 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 6.59 and 6.65 (2H, AB spin system, ^3J = 2.4 Hz, CH=CH), 7.15−7.39 (5H, m, H arom). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) δ: 13.72 (CH_3), 19.83 (CH_2CH_3), 30.95 (NCH_2CH_2S), 31.67 ($NCH_2CH_2CH_2$), 47.43 ($NCH_2CH_2CH_2$), 47.62 (NCH_2CH_2S), 116.33, 117.75 (CH=CH), 125.52 (*C para*-phenyl), 129.11 (*C meta*-phenyl), 129.14 (*C ortho*-phenyl), 134.83 (*C ipso*-phenyl), 161.60 (NCN). MS (ESI): m/z 332.2 $[M + K]^+$.

Synthesis of the Silver Complexes 5·AgI−8·AgI.

5·AgI: R = 2,4,6-trimethylphenyl; R′ = ethyl. The imidazolium iodide **5·HI** (0.080 g, 0.199 mmol) was dissolved in dry CH_2Cl_2, and solid Ag_2O (0.046 g, 0.199 mmol) was added under nitrogen. The reaction mixture was stirred for 2 h in the dark at room temperature. Then the suspension was filtered through a Celite pad, and the solvent was evaporated under reduced pressure to give the product as a light-sensitive white solid. Yield: 88%. Anal. Calcd for $C_{16}H_{22}AgIN_2S$ (509.20): C, 37.74; H, 4.35; N, 5.50. Found: C, 37.55; H, 4.52; N, 5.31. FTIR: ν_{max}(solid)/cm^{-1}: 3116br, 3086br, 2962m, 2914m, 2862br, 2733br, 1607w,1558w, 1545w, 1486m, 1444m, 1408m, 1375w, 1352w, 1300sh, 1259s, 1223m, 1200w, 1152w, 1088s, 1065s, 1015vs, 968sh, 934w, 851m, 797vs, 733vs, 684m, 667m. ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.19 (3H, t, ^3J = 7.4 Hz, SCH_2CH_3), 1.87 (6H, s, 2 CH_3 *ortho*-Mes), 2.33 (3H, s, CH_3 *para*-Mes), 2.46 (2H, q, ^3J = 7.4 Hz, SCH_2CH_3), 2.95 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 4.43 (2H, t, ^3J = 6.3 Hz, NCH_2CH_2S), 6.88 and 7.42 (2H, AB spin system, ^3J = 1.7 Hz, CH=C*H*NCH$_2$ and MesNC*H*=CH), 6.90 (2H, s, 2*H meta*-Mes). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz) δ: 14.89 (SCH_2CH_3), 17.77 (2 CH_3 *ortho*-Mes), 21.16 (CH_3 *para*-Mes), 26.68 (SCH_2CH_3), 33.43 (NCH_2CH_2S), 51.61 (NCH_2CH_2S), 122.04, 122.33 (CH=CH), 129.22 (2 *CH meta*-Mes), 134.90 (2 *C ortho*-Mes), 135.58 (*C ipso*-Mes), 139.16 (*C para*-Mes), 183.26 (NCN). MS (ESI): m/z 381.1 $[M - I]^+$.

The silver cluster $[5\cdot(AgI)_2]_2$ was synthesized using the same procedure, with further addition of AgI (0.047 g, 0.199 mmol).

This compound is poorly soluble in organic solvents. The ^{1}H NMR spectrum recorded shows the same pattern as that of **5**·AgI. The ESI-MS spectrum shows a signal corresponding to $[[\mathbf{5}\cdot(AgI)_2]_2 - I]^+$ in accordance with a structure being partially retained in solution. MS (ESI): m/z 1487.5 $[M - I]^+$. Far FT-IR ν_{max}(crystals)/cm^{-1}: 236vs (μ_2-I), 154vs (μ_3-I).

6·AgI: R = 2,6-diisopropylphenyl; R′ = ethyl. The same procedure was used with **6**·HI (0.110 g, 0.25 mmol) and Ag_2O (0.057 g, 0.25 mmol). The product was isolated as a light-sensitive white solid. Yield: 84%. Anal. Calcd for $C_{19}H_{28}AgIN_2S$ (551.28): C, 41.40; H, 5.12; N, 5.08. Found: C, 41.08; H, 5.26; N, 4.88. FTIR: ν_{max}(solid)/cm^{-1}: 2963m, 2928m, 2870br, 1460m, 1416w, 1386w, 1364w, 1305w, 1261m, 1219w, 1191w, 1105m, 1072m, 1059m, 1024m, 938w, 874sh, 853vs, 806s, 762m, 741m, 691w, 670w. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.92 and 1.06 (2 × 6H, 2 d, ^3J = 6.6 Hz, 2 CH(CH_3)$_2$), 1.18 (3H, t, ^3J = 7.3 Hz, SCH$_2$CH_3), 2.26 (2H, sept, ^3J = 6.8 Hz, 2 CH(CH$_3$)$_2$), 2.49 (2H, q, ^3J = 7.2 Hz, SCH_2CH$_3$), 2.96 (2H, br, NCH$_2$CH_2S), 4.31 (2H, br, NCH_2CH$_2$S), 6.95 and 7.43 (2H, AB spin system, ^3J = 1.5 Hz, CH=CHNCH$_2$ and DiipNCH=CH), 7.17 (2H, d, ^3J = 7.8 Hz, 2H *meta*-Diip), 7.41 (1H, t, ^3J = 7.8 Hz, H *para*-Diip). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz) δ: 14.84 (SCH$_2$CH_3), 24.04, 24.20 (2 CHCH_3), 24.57 (SCH_2CH$_3$), 28.08 (2 CHCH$_3$), 33.49 (NCH$_2$CH_2S), 51.38 (NCH_2CH$_2$S), 124.16, 124.61 (CH=CH), 129.28 (C *ipso*-Diip), 130.41 (CH *meta*-Diip), 134.68 (CH *para*-Diip), 145.82 (C *ortho*-Diip), 181.48 (NCN). MS (ESI): m/z 423.1 $[M - I]^+$.

7·AgI: R = 2,4,6-trimethylphenyl; R′ = phenyl. The same procedure was used with **7**·HI (0.120 g, 0.27 mmol) and Ag_2O (0.062 g, 0.27 mmol). The product was isolated as a light-sensitive white solid. Yield: 91%. Anal. Calcd for $C_{20}H_{22}AgIN_2S$ (557.24): C, 43.11; H, 3.98; N, 5.03. Found: C, 42.73; H, 4.10; N, 4.88. FTIR: ν_{max}(solid)/cm^{-1}: 3150br, 2965m, 2929br, 2871br, 1583w, 1564w, 1549w, 1459m, 1440m, 1415w, 1387w, 1366w, 1309w, 1264w, 1217w, 1188m, 1105m, 1088w, 1072m, 1059m, 1025w, 937w, 875sh, 828vs, 737vs, 692s, 671s. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.79 (6H, s, 2 CH_3 *ortho*-Mes), 2.30 (3H, s, CH_3 *para*-Mes), 3.32 (2H, t, ^3J = 6.0 Hz, NCH$_2$CH_2S), 4.43 (2H, t, ^3J = 6.0 Hz, NCH_2-CH$_2$S), 6.80 and 7.36 (2H, AB spin system, ^3J = 1.6 Hz, CH=CH-NCH$_2$ and MesNCH=CH), 6.84 (2H, s, 2H *meta*-Mes), 7.24−7.26 (5H, m, H aromatics). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz) δ: 17.87 (2 CH$_3$ *ortho*-Mes), 21.21 (CH$_3$ *para*-Mes), 35.62 (NCH$_2$$CH_2$S), 50.94 (N$CH_2CH_2$S), 122.19, 122.53 (CH=CH), 126.60 (CH *para*-Ph), 129.16 (2 CH *meta*-Ph), 129.32 (2 CH *meta*-Mes), 129.42 (2 CH *ortho*-Ph), 134.91 (C *ipso*-Mes), 134.98 (2 C *ortho*-Mes), 135.64 (C *ipso*-Ph), 139.01 (C *para*-Mes), 183.10 (NCN). MS (ESI): m/z 431.1 $[M - I]^+$.

8·AgI: R = 2,6-diisopropylphenyl; R′ = phenyl. The same procedure was used with **8**·HI (0.100 g, 0.20 mmol) and Ag_2O (0.047 g, 0.20 mmol). The product was isolated as a light-sensitive white solid. Yield: 68%. Anal. Calcd for $C_{23}H_{28}AgIN_2S$ (599.32): C, 46.09; H, 4.71; N, 4.67. Found: C, 45.62; H, 4.33; N, 5.04. FTIR: ν_{max}(solid)/cm^{-1}: 3143br, 2962s, 2927m, 2869m, 1591w, 1563w, 1549w, 1458s, 1414s, 1363m, 1261m, 1218w, 1182w, 1105m, 1072m, 1059s, 960w, 938w, 876m, 833vs, 761w, 737m, 687w. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.86 and 1.07 (2 × 6H, 2 d, ^3J = 6.9 Hz, 2 CH(CH_3)$_2$), 2.33 (2H, sept, ^3J = 6.9 Hz, 2 CH(CH$_3$)$_2$), 3.04 (2H, br, NCH$_2$CH_2S), 4.28 (2H, br, NCH_2CH$_2$S), 7.02 and 7.54 (2H, AB spin system, ^3J = 1.8 Hz, CH=CHNCH$_2$ and DiipNCH=CH), 7.13 (2H, d, ^3J = 7.5 Hz, 2H *meta*-Diip), 7.21−7.28 (5H, m, H aromatics), 7.43 (1H, t, ^3J = 7.5 Hz, H *para*-Diip). MS (ESI): m/z 473.1 $[M - I]^+$.

Synthesis of the Mono-NHC Chelated Palladium Dichloride Complexes 10−12. The low solubility of these compounds in organic solvents prevented recording of their ^{13}C{^{1}H} NMR spectra. Two synthetic methods, routes A and B, are detailed below.

Route A: The Transmetalation Reaction. The imidazolium chloride was dissolved in dry CH_2Cl_2, and solid Ag_2O was added under nitrogen. The reaction mixture was stirred for 2 h in the dark at room temperature. Then the suspension was filtered through a Celite pad under nitrogen, and the resulting clear solution was slowly added to a suspension of the desired palladium precursor. A white solid precipitated rapidly. The suspension was then filtered through Celite, and the solvent was evaporated under reduced pressure. The resulting solid was then washed with pentane (2 × 25 mL) and crystallized from a dichloromethane/pentane solution.

Route B: *In Situ* Deprotonation of a Zwitterionic Intermediate. The zwitterionic precursor (see below complexes **13**−**16**) and Cs_2CO_3 were placed in a Schlenk tube under nitrogen, and MeCN was added. The reaction mixture was heated at 60 °C for 3 h and then allowed to cool to room temperature. After filtration through a Celite pad, the solvent was evaporated under reduced pressure. The resulting solid was washed with pentane (2 × 20 mL) and recrystallized from a dichloromethane/pentane solution.

Synthesis of **9**: R = methyl; R′ = ethyl.

Route A: see ref 18d.

Route B: Zwitterion **13** (0.070 g, 0.18 mmol) and Cs_2CO_3 (0.059 g, 0.18 mmol). The product was isolated as a yellow solid. Yield: 76%.

Synthesis of **10**: R = *n*-butyl; R′ = ethyl.

Route A: **2**·HCl (0.250 g, 1.00 mmol), Ag_2O (0.233 g, 1.00 mmol), and $[PdCl_2(cod)]$ (0.287 g, 1.00 mmol). The product was isolated as a yellow solid. Yield: 80%. Anal. Calcd for $C_{11}H_{20}Cl_2N_2PdS$ (389.68): C, 33.90; H, 5.17; N, 7.19. Found: C, 33.32; H, 5.44; N, 6.87. FTIR: ν_{max}(solid)/cm^{-1}: 3162w, 3124w, 3097w, 3047w, 2958m, 2940m, 2930m, 2869w, 1581w, 1572w, 1550w, 1479w, 1460m, 1438m, 1420s, 1381w, 1354w, 1275m, 1231s, 1202w, 1158w, 1129w, 1107w, 1107w, 1087w, 1074w, 1022m, 960w, 895w, 869w, 833w, 826w, 799w, 758m, 735vs, 726vs, 704vs, 688vs, 669s, 312vs (ν_{Pd-Cl}), 296vs (ν_{Pd-Cl}). ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 0.98 (3H, t, ^3J = 7.5 Hz, CH_3 butyl), 1.40 (5H, m, SCH$_2$CH_3 and NCH$_2$CH$_2$CH_2CH$_3$), 1.91 (2H, m, NCH$_2$CH_2CH$_2$CH$_3$), 2.55 (2H, br, SCH_2CH$_3$), 2.89 (2H, br, NCH$_2$CH_2S), 4.52 (4H, br, NCH_2CH$_2$S and NCH_2-CH$_2$CH$_2$CH$_3$), 7.01 and 7.20 (2H, AB spin system, ^3J = 1.8 Hz, CH=CH). MS (ESI): m/z 355.0 $[M - Cl]^+$.

Route B: Zwitterion **14** (0.100 g, 0.23 mmol) and Cs_2CO_3 (0.076 g, 0.23 mmol). Yield: 74%.

Synthesis of **11**: R = methyl; R′ = phenyl.

Route A: **3**·HCl (0.250 g, 0.98 mmol), Ag_2O (0.227 g, 0.98 mmol), and $[PdCl_2(cod)]$ (0.280 g, 0.98 mmol). The product was isolated as a yellow solid. Yield: 77%. Anal. Calcd for $C_{12}H_{14}Cl_2N_2PdS$ (395.64): C, 36.43; H, 3.57; N, 7.08. Found: C, 35.78; H, 3.22; N, 7.42. FTIR: ν_{max}(solid)/cm^{-1}: 3162w, 3124w, 3055w, 2946br, 1582w, 1572w, 1479w, 1466m, 1438s, 1405m, 1356w, 1337w, 1279w, 1230s, 1185sh, 1161w, 1120sh, 1087m, 1023m, 977w, 893w, 835w, 765sh, 742s, 727vs, 700s, 686vs, 672s, 311vs (ν_{Pd-Cl}), 296vs (ν_{Pd-Cl}). ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 3.06 (2H, br, NCH$_2$CH_2S), 3.91 (3H, br s, CH_3), 4.63 (2H, br, NCH_2CH$_2$S), 6.88 (1H, br s, CH=CH), 7.04 (1H, br s, CH=CH), 7.37−7.45 (5H, m, H phenyl). MS (ESI): m/z 361.0 $[M - Cl]^+$.

Route B: Zwitterion **15** (0.100 g, 0.23 mmol) and Cs_2CO_3 (0.75 g, 0.23 mmol). Yield: 71%.

Synthesis of **12**: R = *n*-butyl; R′ = phenyl.

Route A: **4**·HCl (0.250 g, 0.84 mmol), Ag_2O (0.195 g, 0.84 mmol), and $[PdCl_2(cod)]$ (0.240 g, 0.84 mmol). The product was isolated as a yellow solid. Yield: 84%. Anal. Calcd for $C_{15}H_{20}Cl_2N_2PdS$ (437.72): C, 41.16; H, 4.61; N, 6.40. Found: C, 41.48; H, 4.39; N, 6.09. FTIR: ν_{max}(solid)/cm^{-1}: 3158w, 3128w, 3099w, 3058w, 2956m, 2929m, 2870w, 1734w, 1719w, 1580w, 1563w, 1472m, 1457m, 1441s, 1425s, 1414m, 1377w, 1356w, 1336w, 1283w, 1240m, 1218w, 1197w, 1159w, 1134w, 1109w, 1059w, 1024w, 999w, 955w, 870w, 739vs, 708w, 686vs, 295vs (ν_{Pd-Cl}). ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 0.88 (3H, t, ^3J = 7.3 Hz, CH_3), 1.29 (2H, m, CH_2CH$_3$), 1.65 (2H, br m, CH_2CH$_2$CH$_3$), 3.17 (2H, br, NCH$_2$CH_2S), 4.44 (2H, br, NCH_2CH$_2$CH$_2$), 4.65 (2H, br, NCH_2CH$_2$S), 7.00 (1H,

br s, C*H*=CH), 7.18 (H, br s, CH=C*H*), 7.37−7.45 (5H, m, H phenyl). MS (ESI): *m*/*z* 403.0 $[M - Cl]^+$.

Route B: Zwitterion **16** (0.120 g, 0.25 mmol) and Cs_2CO_3 (0.082 g, 0.25 mmol). Yield: 69%.

Synthesis of the Zwitterionic Palladium Complexes 13−16. Because of their low solubility in organic solvents, recording of the $^{13}C\{^1H\}$ NMR spectra of complexes **13**−**15** was prevented.

13: R = methyl; R′ = ethyl. Solid $[PdCl_2(cod)]$ (0.276 g, 0.97 mmol) was added to a solution of **1**·HCl (0.200 g, 0.97 mmol) in dichloromethane. The reaction mixture was stirred for 2 h at room temperature, until a yellow precipitate appeared. The solvent was removed via canula, and the solid was washed with pentane (2 × 20 mL) and dried under vacuum. The product was isolated as a yellow solid. Yield: 87%. Anal. Calcd for $C_8H_{15}Cl_3N_2PdS$ (384.06): C, 25.02; H, 3.94; N, 7.29. Found: C, 25.30; H, 3.64; N, 7.44. FTIR: ν_{max}(solid)/cm^{-1}: 3160w, 3090s, 3071s, 3007w, 2958w, 2924sh, 2942w, 2866w, 1639w, 1574m, 1558s, 1450s, 1427s, 1375m, 1330w, 1314w, 1285w, 1272w, 1250w, 1225m, 1165vs, 1122m, 1090sh, 1061m, 1046w, 1016m, 991w, 970w, 856vs, 798m, 767vs, 752s, 711w, 347vs (ν_{Pd-Cl}), 306vs (ν_{Pd-Cl}), 286vs (ν_{Pd-Cl}). ^1H NMR (d_6-DMSO, 300 MHz) δ: 1.19 (3H, t, ^3J = 7.5 Hz, SCH_2CH_3), 2.57 (overlapped with solvent peak, SCH_2CH_3), 2.99 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 3.89 (3H, s, NCH_3), 4.37 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 7.73 (1H, br s, C*H*=CH), 7.82 (1H, br s, CH=C*H*), 9.22 (1H, br s, NCHN). MS (ESI): *m*/*z* 407.9 $[M + Na]^+$, 348.9 $[M - Cl]^+$.

14: R = *n*-butyl; R′ = ethyl.

The same procedure was used with $[PdCl_2(cod)]$ (0.229 g, 0.80 mmol) and **2**·HCl (0.200 g, 0.80 mmol). The product was isolated as a yellow solid. Yield: 89%. Anal. Calcd for $C_{11}H_{21}Cl_3N_2PdS$ (426.14): C, 31.00; H, 4.97; N, 6.57. Found: C, 30.31; H, 5.17; N, 6.09. FTIR: ν_{max}(solid)/cm^{-1}: 3136br, 3103s, 3078m, 2964m, 2930m, 2875br, 2861br, 1620w, 1564vs, 1451s, 1414s; 1405m, 1371m, 1355m, 1338w, 1308m, 1299w, 1268m, 1245w, 1226w, 1205w, 1178vs, 1157vs, 1122w, 1111w, 1069w, 1041w, 1005w, 956w, 891w, 838vs, 825s, 780m, 756vs, 749s, 344vs (ν_{Pd-Cl}), 312vs (ν_{Pd-Cl}), 286vs (ν_{Pd-Cl}). ^1H NMR (d_6-DMSO, 300 MHz) δ: 0.90 (3H, t, ^3J = 7.5 Hz, CH_3 butyl), 1.17 (3H, t, ^3J = 7.5 Hz, SCH_2CH_3), 1.26 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.78 (2H, m, $NCH_2CH_2CH_2CH_3$), 2.54 (overlapped with solvent peak, SCH_2CH_3), 2.90 (2H, t, ^3J = 6.0 Hz, NCH_2CH_2S), 4.20 (2H, t, ^3J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 4.36 (2H, t, ^3J = 6.3 Hz, NCH_2CH_2S), 7.81 (2H, br s, CH=CH), 9.23 (1H, br s, NCHN). MS (ESI): *m*/*z* 450.0 $[M + Na]^+$, 392.0 $[M - Cl]^+$.

15: R = methyl; R′ = phenyl.

The same procedure was used with $[PdCl_2(cod)]$ (0.224 g, 0.79 mmol) and **3**·HCl (0.200 g, 0.79 mmol). The product was isolated as a yellow solid. Yield: 84%. Anal. Calcd for $C_{12}H_{15}Cl_3N_2PdS$ (432.10): C, 33.35; H, 3.50; N, 6.48. Found: C, 32.94; H, 3.39; N, 7.01. FTIR: ν_{max}(solid)/cm^{-1}: 3155br, 3123w, 3111m, 3075m, 2982m, 2935w, 1618w, 1572m, 1479w, 1450w, 1443m, 1432m, 1423sh, 1404w, 1352m, 1313m, 1299m, 1275w, 1248w, 1176vs, 1170vs, 1110m, 1072w, 1047w, 1020w, 1000w, 954w, 924w, 890w, 838s, 753vs, 690vs, 668w, 335vs (ν_{Pd-Cl}), 306vs (ν_{Pd-Cl}), 287vs (ν_{Pd-Cl}). ^1H NMR (d_6-DMSO, 300 MHz) δ: 3.49 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 3.81 (3H, s, NCH_3), 4.38 (2H, t, ^3J = 6.6 Hz, NCH_2CH_2S), 7.23−7.40 (5H, m, H phenyl), 7.62 (1H, br s, C*H*=CH), 7.74 (1H, br s, CH=C*H*), 9.10 (1H, br s, NCHN). MS (ESI): *m*/*z* 455.9 $[M + Na]^+$, 397.9 $[M - Cl]^+$.

16: R = *n*-butyl; R′ = phenyl.

The same procedure was used with $[PdCl_2(cod)]$ (0.192 g, 0.67 mmol) and **4**·HCl (0.200 g, 0.67 mmol). The product was isolated as a yellow solid. Yield: 81%. Anal. Calcd for $C_{15}H_{21}Cl_3N_2PdS$ (474.18): C, 37.99; H, 4.46; N, 5.91. Found: C, 37.48; H, 4.23; N, 5.70. FTIR: ν_{max}(solid)/cm^{-1}: 3130w, 3100m, 3056m, 2984sh, 2954sh, 2934w, 2859br, 1619w, 1577w, 1562s, 1468w, 1453m, 1440s, 1411w, 1382w, 1367w, 1346w, 1333w, 1311w, 1300w, 1249w, 1215w, 1207w, 1169s, 1151s, 1113w, 1101w, 1071w, 1041sh, 1022w, 1001w, 967w, 949w, 917w, 895sh, 882w, 855m, 826sh, 806sh, 743vs, 688s, 332vs (ν_{Pd-Cl}), 305vs (ν_{Pd-Cl}), 287vs (ν_{Pd-Cl}). ^1H NMR (d_6-DMSO, 300 MHz) δ: 0.90 (3H, t, ^3J = 7.5 Hz, CH_3 butyl), 1.25 (2H, m, CH_2CH_3), 1.73 (2H, m, $CH_2CH_2CH_3$), 3.50 (2H, t, ^3J = 6.3 Hz, NCH_2CH_2S), 4.13 (2H, t, ^3J = 7.2 Hz, $NCH_2CH_2CH_2$), 4.38 (2H, t, ^3J = 6.3 Hz, NCH_2CH_2S), 7.22−7.39 (5H, m, H phenyl), 7.74 (1H, pseudo t, $^3J = {}^4J$ = 1.5 Hz, C*H*=CH), 7.79 (1H, pseudo t, $^3J = {}^4J$ = 1.5 Hz, CH=C*H*), 9.18 (1H, br s, NCHN). $^{13}C\{^1H\}$ NMR (d_6-DMSO, 75.5 MHz) δ: 13.75 (CH_3), 19.20 ($NCH_2CH_2CH_2CH_3$), 31.75 (NCH_2CH_2S), 32.69 ($NCH_2CH_2CH_2CH_3$), 48.33 ($NCH_2CH_2CH_2CH_3$), 49.02 (NCH_2CH_2S), 122.84, 123.11 (CH=CH), 126.99 (*C para*-phenyl), 129.32 (*C meta*-phenyl), 129.70 (*C ortho*-phenyl), 136.86 (*C ipso*-phenyl), NCN resonance not observed. MS (ESI): *m*/*z* 498.0 $[M + Na]^+$, 440.0 $[M - Cl]^+$.

Synthesis of the Bis-NHC Palladium Dichloride Complexes 18−20. The transmetalation reaction procedure described above (route A) was followed for these complexes.

18: R = *n*-butyl; R′ = ethyl.

2·HCl (0.200 g, 0.80 mmol), Ag_2O (0.186 g, 0.80 mmol), and $[PdCl_2(cod)]$ (0.115 g, 0.40 mmol). The product was isolated as a yellow solid. Yield: 74%. Anal. Calcd for $C_{22}H_{40}Cl_2N_4PdS_2$ (602.03): C, 43.89; H, 6.70; N, 9.31. Found: C, 43.48; H, 6.44; N, 9.62. FTIR: ν_{max}(solid)/cm^{-1}: 3163br, 3126br, 3048br, 2959br, 2940br, 2872br, 2360w, 2162w, 2050w, 1582w, 1479m, 1461m, 1439m, 1421s, 1381m, 1355m, 1276m, 1232m, 1203w, 1159w, 1130w, 1107w, 1088w, 1024m, 935w, 896w, 871w, 833w, 800w, 759m, 736vs, 728vs, 705vs, 689vs, 669m, 340vs (ν_{Pd-Cl}). ^1H NMR (CD_2Cl_2, 300 MHz) δ: 1.05 (3H, t, ^3J = 7.5 Hz, CH_3 butyl), 1.23 (3H, t, ^3J = 7.5 Hz, SCH_2CH_3), 1.51 (2H, m, $NCH_2CH_2CH_2CH_3$), 2.01 (2H, m, $NCH_2CH_2CH_2CH_3$), 2.69 (2H, q, ^3J = 7.5 Hz, SCH_2CH_3), 3.53 (2H, br, NCH_2CH_2S), 4.51 (2H, q, ^3J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$), 4.66 (2H, br, NCH_2CH_2S), 6.91 and 7.09 (2H, AB spin system, ^3J = 1.8 Hz, CH=CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 300 MHz) δ: 13.73 (CH_3 butyl), 14.75 (SCH_2CH_3), 20.04 ($NCH_2CH_2CH_2CH_3$), 26.18 (SCH_2CH_3), 31.08 (NCH_2CH_2S), 32.07 ($NCH_2CH_2CH_2CH_3$), 50.72 ($NCH_2CH_2CH_2CH_3$), 51.00 (NCH_2CH_2S), 118.93, 121.51 (CH=CH), NCN resonance not observed. MS (ESI): *m*/*z* 568.2 $[M - Cl]^+$.

19: R = methyl; R′ = phenyl.

3·HCl (0.200 g, 0.79 mmol), Ag_2O (0.182 g, 0.79 mmol), and $[PdCl_2(cod)]$ (0.112 g, 0.39 mmol). The product was isolated as a yellow solid. Yield: 72%. Anal. Calcd for $C_{24}H_{28}Cl_2N_4PdS_2$ (613.96): C, 46.95; H, 4.60; N, 9.13. Found: C, 50.24; H, 4.58; N, 9.41. FTIR: ν_{max}(solid)/cm^{-1}: 3161br, 3124br, 3098br, 3055br, 2947br, 1582w, 1572w, 1535w, 1479w, 1467m, 1439m, 1406m, 1356w, 1338w, 1279w, 1260w, 1230m, 1162w, 1087s, 1022s, 953w, 893w, 875w, 834w, 798m, 742s, 727vs, 698s, 687vs, 657w, 337vs (ν_{Pd-Cl}). ^1H NMR (CD_2Cl_2, 300 MHz) δ: 3.72 (2H, t, ^3J = 6.9 Hz, NCH_2CH_2S), 4.08 (3H, s, NCH_3), 4.65 (2H, t, ^3J = 6.9 Hz, NCH_2CH_2S), 6.82 and 6.88 (2H, AB spin system, ^3J = 1.8 Hz, CH=CH), 7.18−7.46 (5H, m, H phenyl). MS (ESI): *m*/*z* 580.1 $[M - Cl]^+$.

20: R = *n*-butyl; R′ = phenyl.

4·HCl (0.200 g, 0.67 mmol), Ag_2O (0.156 g, 0.67 mmol), and $[PdCl_2(cod)]$ (0.096 g, 0.34 mmol). The product was isolated as a yellow solid. Yield: 76%. Anal. Calcd for $C_{30}H_{40}Cl_2N_4PdS_2$ (698.12): C, 51.61; H, 5.78; N, 8.03. Found: C, 52.02; H, 5.39; N, 7.66. FTIR: ν_{max}(solid)/cm^{-1}: 3158br, 3123br, 3096br, 3055br, 2957s, 2929s, 2871m, 1582m, 1480m, 1464m, 1439m, 1423m, 1378w, 1356w, 1278w, 1232m, 1202w, 1158w, 1132w, 1088w, 1041w, 1024w, 736vs, 703s, 691vs, 668w, 347vs (ν_{Pd-Cl}). ^1H NMR (CD_2Cl_2, 300 MHz) δ: 0.99 (3H, t, ^3J = 7.2 Hz, CH_3 butyl), 1.45 (2H, m, $NCH_2CH_2CH_2CH_3$), 2.05 (2H, m, $NCH_2CH_2CH_2CH_3$), 3.72 (2H, q, ^3J = 6.9 Hz, NCH_2CH_2S), 4.46 (2H, q, ^3J = 7.5 Hz, $NCH_2CH_2CH_2CH_3$), 4.68 (2H, q, ^3J = 6.9 Hz, NCH_2CH_2S), 6.82 and 6.88 (2H, AB spin system, ^3J = 1.8 Hz, CH=CH), 7.16−7.42 (5H, m, H phenyl). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz) δ: 13.60 (CH_3), 20.07 ($NCH_2CH_2CH_2CH_3$), 33.04 (NCH_2CH_2S), 34.33 ($NCH_2CH_2CH_2CH_3$), 49.91

($NCH_2CH_2CH_2CH_3$), 50.58 (NCH_2CH_2S), 120.37, 121.41 (CH=CH), 126.24 (*C para*-phenyl), 129.09 (*C meta*-phenyl), 129.23 (*C ortho*-phenyl), 135.13 (*C ipso*-phenyl), 170.10 (NCN). MS (ESI): m/z 664.2 $[M - Cl]^+$.

Synthesis of the Bis-NHC Dicationic Palladium Complexes 21−24. The transmetalation reaction procedure described above (route A) was followed for these complexes.

21: R = methyl; R′ = ethyl.

1·HCl (0.200 g, 0.97 mmol), Ag_2O (0.224 g, 0.97 mmol), and $[Pd(NCMe)_4][BF_4]_2$ (0.215 g, 0.48 mmol). The product was isolated as a light brown solid. Yield: 68%. Anal. Calcd for $C_{16}H_{28}B_2F_8N_4PdS_2$ (620.58): C, 30.97; H, 4.55; N, 9.03. Found: C, 30.39; H, 5.04; N, 8.76. FTIR: ν_{max}(solid)/cm^{-1}: 3166br, 3140br, 2966br, 2933br, 1628br, 1568w, 1543w, 1527w, 1474m, 1453m, 1411m, 1381w, 1363w, 1337w, 1286w, 1268w, 1244w, 1214w, 1172w, 1030vs, 877w, 848w, 752s, 688m, 679m, 659w. ^{1}H NMR (CD_3CN, 300 MHz) δ: 1.23 (3H, t, ^3J = 6.9 Hz, SCH_2CH_3), 2.67 (2H, br, SCH_2CH_3), 2.96 (2H, br, NCH_2CH_2S), 3.86 (3H, s, NCH_3), 4.45 (2H, br, NCH_2CH_2S), 7.18 (1H, br s, CH=CH), 7.32 (1H, br s, CH=CH). ^{13}C{^{1}H} NMR (CD_3CN, 75 MHz) δ: 13.38 (SCH_2CH_3), 32.36 (SCH_2CH_3), 32.25 (NCH_2CH_2S), 38.20 (NCH_3), 50.59 (NCH_2CH_2S), 124.33, 125.86 (CH=CH), 157.82 (NCN).

22: R = *n*-butyl; R′ = ethyl.

2·HCl (0.200 g, 0.80 mmol), Ag_2O (0.186 g, 0.80 mmol), and $[Pd(NCMe)_4][BF_4]_2$ (0.179 g, 0.40 mmol). The product was isolated as a light brown solid. Yield: 67%. Anal. Calcd for $C_{22}H_{40}B_2F_8N_4PdS_2$ (704.74): C, 37.49; H, 5.72; N, 7.95. Found: C, 37.01; H, 5.30; N, 8.34. FTIR: ν_{max}(solid)/cm^{-1}: 3144br, 3112sh, 2961m, 2933m, 2874w, 1623br, 1565w, 1533w, 1457m, 1427m, 1379w, 1354w, 1241w, 1201w, 1162m, 1047vs, 1033vs, 875w, 849w, 750s, 691m. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 0.85 (3H, t, ^3J = 7.5 Hz, CH_3 butyl), 1.20 (3 h, t, ^3J = 7.5 Hz, SCH_2CH_3), 1.35 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.84 (2H, m, $NCH_2CH_2CH_2CH_3$), 2.53 (2H, br q, SCH_2CH_3), 2.95 (2H, br t, NCH_2CH_2S), 4.17 (2H, br t, $NCH_2CH_2CH_2CH_3$), 4.37 (2H, br t, NCH_2CH_2S), 7.15 (2H, br s, CH=CH). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz) δ: 13.30 (CH_3 butyl), 14.19 (SCH_2CH_3), 19.79 ($NCH_2CH_2CH_2CH_3$), 25.62 (SCH_2CH_3), 31.35 (NCH_2CH_2S), 32.44 ($NCH_2CH_2CH_2CH_3$), 49.83 ($NCH_2CH_2CH_2CH_3$), 50.90 (NCH_2CH_2S), 122.64, 122.72 (CH=CH), 157.06 (NCN).

23: R = methyl; R′ = phenyl.

3·HCl (0.200 g, 0.79 mmol), Ag_2O (0.182 g, 0.79 mmol), and $[Pd(NCMe)_4][BF_4]_2$ (0.174 g, 0.39 mmol). The product was isolated as a light brown solid. Yield: 64%. Anal. Calcd for $C_{24}H_{28}B_2F_8N_4PdS_2$ (716.66): C, 40.22; H, 3.94; N, 7.82. Found: C, 40.68; H, 3.69; N, 8.16. FTIR: ν_{max}(solid)/cm^{-1}: 3168w, 3141w, 2956w, 2922w, 2851w, 1577w 1544w, 1473m, 1442m, 1408m, 1359w, 1337w, 1284w, 1241w, 1206w, 1171w, 1031vs, 999vs, 887m, 847w, 742s, 686s. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 3.37 (2H, br t, NCH_2CH_2S), 4.33 (2H, br, NCH_2CH_2S), 4.84 (3H, br s, CH_3), 7.02−7.42 (7H, m, CH=CH and H phenyl). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz) δ: 33.75 (NCH_2CH_2S), 37.54 (NCH_3), 51.38 (NCH_2CH_2S), 123.42, 123.54 (CH=CH), 127.21 (*C para*-phenyl), 129.38 (*C meta*-phenyl), 130.18 (*C ortho*-phenyl), 132.90 (*C ipso*-phenyl), 155.20 (NCN).

24: R = *n*-butyl; R′ = phenyl.

4·HCl (0.200 g, 0.67 mmol), Ag_2O (0.156 g, 0.67 mmol), and $[Pd(NCMe)_4][BF_4]_2$ (0.150 g, 0.34 mmol). The product was isolated as a light brown solid. Yield: 71%. Anal. Calcd for $C_{30}H_{40}B_2F_8N_4PdS_2$ (800.82): C, 44.99; H, 5.03; N, 7.00. Found: C, 45.39; H, 5.14; N, 6.67. FTIR: ν_{max}(solid)/cm^{-1}: 3149br, 3112sh, 2960w, 2932w, 2873w, 2113w, 1724w, 1564w, 1473m, 1458sh, 1442m, 1430w, 1381w, 1356w, 1338w, 1285w, 1242w, 1163w, 1049vs, 1034vs, 1000s, 846w, 745s, 688m. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 0.91 (3H, t, ^3J = 7.3 Hz, CH_3), 1.30 (2H, m, CH_2CH_3), 1.78 (2H, br m, $CH_2CH_2CH_3$), 3.66 (2H, br, NCH_2CH_2S), 4.45 (2H, br, $NCH_2CH_2CH_2$), 4.78 (2H, br, NCH_2CH_2S), 7.23−7.45 (7H, m, CH=CH and H phenyl). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz) δ: 15.08 (CH_3), 21.26 ($NCH_2CH_2CH_2CH_3$), 33.67 (NCH_2CH_2S), 34.95 ($NCH_2CH_2CH_2CH_3$), 51.82 ($NCH_2CH_2CH_2CH_3$), 52.76 (NCH_2CH_2S), 124.27, 125.38 (CH=CH), 130.96 (*C para*-phenyl), 131.70 (*C meta*-phenyl), 132.18 (*C ortho*-phenyl), 132.41 (*C ipso*-phenyl), NCN resonance not observed.

General Procedure for the Suzuki−Miyaura Cross-Coupling Reaction. The catalyst precursor (0.02 mmol), phenyl boronic acid (146.3 mg, 1.20 mmol), and Cs_2CO_3 (651.6 mg, 2.00 mmol) were placed in a Schlenk tube, and DMSO (3 mL) was added under nitrogen. Then 4-bromotoluene (123.1 μL, 171.0 mg, 1.00 mmol) was added, and the reaction mixture was heated for 2 h at 60 °C. The reaction was then quenched by rapid cooling to room temperature, and the suspension was filtered through a Celite pad. The resulting solution was then analyzed by gas chromatography. All runs were repeated two times, and the value reported is an average of the two yields measured. The corresponding yields in 4-methylbiphenyl are reported in Tables 1 and 3.

The same procedure was used with different solvents (3 mL) or different bases (2.00 mmol), and the corresponding yields in 4-methyl-biphenyl are reported in Table 2.

The same procedure was used with catalyst (0.01 mmol) or 4-chlorotoluene (118.3 μL, 126.6 mg, 1.00 mmol) as reagent instead of 4-bromotoluene, and the corresponding yields in 4-methyl-biphenyl are reported in Table 4.

X-ray Data Collection, Structure Solution, and Refinement for All Compounds. Suitable crystals for the X-ray analysis of all compounds were obtained as described above. The intensity data were collected on a Kappa CCD diffractometer[32] (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å) at 173(2) K. Crystallographic and experimental details for the structures are summarized in Table 1. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[33] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined *riding* on the corresponding parent atoms, except for the H1 atom in the structure of **8**·HPF_6. For **8**·HPF_6, the PF_6 anion was found disordered in two positions with equal occupancy factors and with a F−P−F axis in common. The disorder could be refined unrestrained. For $[\mathbf{5}\cdot(AgI)_2]_2$, the mesityl group was disordered with very close images. It was not possible to define the atomic coordinates for the two images of this disorder. Instead, this group was refined with restrained anisotropic parameters. A MULTI-SCAN correction was applied.[34] CCDC 778208−778212 contain the supplementary crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgment. We thank Gilles Schnee (University of Strasbourg) and Alessandra Sabbatini (University of Camerino, Italy) for their contribution to this work and Marc Mermillon-Fournier and Mélanie Boucher for technical assistance. We are most grateful to Dr. Roberto Pattacini for the resolution of the X-ray structures and to the CNRS, the Ministère de la Recherche (Paris), and the DFH/UFA (International Research Training Group 532-GRK532) for funding.

Supporting Information Available: Table S-1 with the crystallographic data and CIF files for all the structures. This material is available free of charge via the Internet at http://pubs.acs.org.

(32) Bruker-Nonius. *Kappa CCD Reference Manual*; Nonius BV: The Netherlands, 1998.

(33) Sheldrick, G. M. *Acta Crystallogr*. **2008**, *A64*, 112–122.

(34) Spek, L. *J. Appl. Crystallogr*. **2003**, *36*, 7. Blessing, B. *Acta Crystallogr*. **1995**, *A51*, 33.