Investigations into the Stability of Tethered Palladium(II) Pincer Complexes during Heck Catalysis

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Received December 19, 2004

A variety of palladated PCP pincer complexes are covalently tethered onto polymeric and silica supports via either amide or ether linkages and are evaluated in the Heck reaction of iodobenzene and *n*-butyl acrylate. The decomposition under reaction conditions of all complexes studied is established through poisoning and kinetic studies. Furthermore, the initial steps of the decomposition pathway of PCP as well as SCS pincer Pd(II) complexes are proposed and validated using in situ NMR, mass spectroscopy, and XAS as well as computational methods. These findings together with our previous reports strongly suggest that all Pd(II) pincer complexes are simply precatalysts during the Heck reaction that decompose to form catalytically active Pd(0) species.

Introduction

The Heck reaction is among the most important and widely used reactions for the formation of carbon−carbon bonds.[1−19] In this reaction, a new bond is created between two sp^2 carbon centers that stem from an alkene and an aryl halide. First reported in the early 1970s by Heck and Mizoroki independently,[20,21] the use of this catalytic reaction has rapidly increased, as a result of its importance in the pharmaceutical and fine chemical industries.[22] A large variety of palladium complexes have been reported that "catalyze" this transformation. These complexes include palladacycles,[23−31] Pd−carbenes,[32−39] and Pd−pincer complex soluble palladium nanoparticles.[19,40−53] While use of these catalytic or precatalytic moieties has been suc-

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(1) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.
(2) Brase, S.; deMeijere, A.; Diederich, F. In *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: New York, 1998.
(3) Cabri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2.
(4) Dieck, H. A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1133.
(5) Dieck, H. A.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 1083.
(6) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: London, 1985.
(7) Heck, R. F. *Org. React.* **1982**, *27*, 345.
(8) Malleron, J. L.; Fiaud, J. C.; Legros, J. Y. *Handbook of Palladium-Catalyzed Organic Reactions: Synthesis Aspects and Catalytic Cycles*; Academic Press: San Diego, CA, 1997.
(9) Link, J. T.; Overman, L. E. *CHEMTECH* **1998**, *28*, 19.
(10) Link, J. T.; Overman, L. E. In *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: New York, 1998.
(11) Crisp, G. T. *Chem. Soc. Rev.* **1998**, *27*, 427.
(12) Tietze, L. F.; Ila, H.; Bell, H. P. *Chem. Rev.* **2004**, *104*, 3453.
(13) Tsuji, J. *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*; Wiley: Chichester, U.K., 1995.
(14) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.
(15) Ritter, K. *Synthesis* **1993**, 735.
(16) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
(17) Farina, V. *Adv. Synth. Catal.* **2004**, *346*, 1553.
(18) DeMeijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379.
(19) Amatore, C.; Jutand, A. *J. Organomet. Chem.* **1999**, *576*, 254.
(20) Mizoroki, T.; Mori, K.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581.
(21) Heck, R. F.; Nolley, J. P. *J. Org. Chem.* **1972**, *37*, 2320.
(22) Blaser, H.-U.; Indolese, A.; Naud, F.; Nettekoven, U.; Schnyder, A. *Adv. Synth. Catal.* **2004**, *346*, 1583.
(23) Beller, M.; Fischer, H.; Herrmann, W. A.; Öfele, K.; Brossmer, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1848.
(24) Beller, M.; Riermeier, T. H.; Haber, S.; Kleiner, H.-J.; Herrmann, W. A. *Chem. Ber.* **1996**.
(25) Beller, M.; Riermeier, T. H. *Eur. J. Inorg. Chem.* **1998**, 29.
(26) Beller, M.; Riermeier, T. H.; Magerlein, W.; Muller, T. E.; Scherer, W. *Polyhedron* **1998**, *17*, 1165.
(27) Hermann, W. A.; Bohm, V. P. W.; Reisinger, C. P. *J. Organomet. Chem.* **1999**, *576*, 23.
(28) Herrmann, W. A.; Brossmer, C.; Öfele, K.; Reisinger, C. P.; Priermeier, T.; Beller, M.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1844.
(29) Herrmann, W. A.; Brossmer, C.; Reisinger, C.-P.; Öfele, K.; Beller, M.; Riermeier, T. H. *Chem. Eur. J.* **1997**, *3*, 1357.
(30) Louie, J.; Hartwig, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2359.
(31) Nowotny, M.; Hanefeld, U.; van Koningsveld, H.; Maschmeyer, T. *Chem. Commun.* **2000**, 1877−1878.
(32) Andrus, M. B.; Song, C.; Zhang, J. *Org. Lett.* **2002**, *4*, 2079.
(33) Steel, P. G.; Teasdale, C. W. T. *Tetrahedron Lett.* **2004**, *45*, 8977.
(34) Yang, C.; Lee, H. M.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1511.
(35) Andrus, M. B.; Song, C.; Zhang, J. *Org. Lett.* **2002**, *4*, 2079.
(36) Loch, J. A.; Albrecht, M.; Peris, E.; Mata, J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 700.
(37) Lebel, H.; Janes, M. K.; Charette, A. B.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5046.
(38) Lee, H. M.; Lu, C. Y.; Chen, C. Y.; Chen, W. L.; Lin, H. C.; Chiu, P. L.; Cheng, P. Y. *Tetrahedron* **2004**, *60*, 5807.
(39) Herrmann, W. A.; Reisinger, C. P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93.
(40) Le Bars, J.; Specht, U.; Bradley, J. S.; Blackmond, D. G. *Langmuir* **1999**, *15*, 7621.
(41) Calo, V.; Nacci, A.; Monopoli, A.; Detomaso, A.; Iliade, P. *Organometallics* **2003**, *22*, 4193.
(42) Galow, T. H.; Drechsler, U.; Hanson, J. A.; Rotello, V. M. *Chem. Commun.* **2002**, 1076.
(43) Gopidas, K. R.; Whitesell, J. K.; Fox, M. A. *Nano Lett.* **2003**, *3*, 1757.
(44) Mandal, S.; Roy, D.; Chaudhari, R. V.; Sastry, M. *Chem. Mater.* **2004**, *16*, 3714.

10.1021/om048992v CCC: $30.25
Publication on Web 07/27/2005

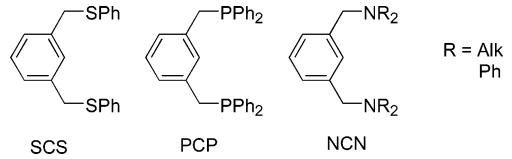


Figure 1. Commonly used types of pincer ligands.

cessful, several factors may limit widespread application of the Heck reaction commercially, including the lack of recovery of expensive palladium species, the use of toxic phosphines during the catalysis, and the difficulty in removing these toxic species from the final products. Several possibilities to overcome these shortcomings have been proposed, including the use of supported catalysts that could be removed easily from the reaction mixture and potentially be reused.[54−61] Among the most attractive palladium−ligand systems that have been supported is the Pd−pincer system.[54,57,58,62−66] Use of these species for Heck reactions results in rapid conversion of substrate, and metal complexes based on pincer ligands have been suggested to be extremely stable.[67,68] Pincer ligands are defined as a tridentate structure bound to a metal. In this work our ligand can be defined as 1,3-disubstituted benzenes with heteroatoms in the side-chains that are able to chelate to the metal center (Figure 1). They are abbreviated by the three atoms that coordinate to the metal center: e.g., SCS, PCP, or NCN pincer.

Over the past decade, extensive work has been carried out on metalated pincer ligands.[54,57,58,62,67,69−73] Advantages of pincer ligands that have been suggested in the literature include an unprecedented stability at high temperatures, making them the candidate of choice for supported catalysis.[67,68] Among the most studied pincer ligands are the ones outlined in Figure 1. When metalated with a typical palladium source, all three pincer ligands contain a Pd(II) metal center. On the basis of this fact and their suggested stability, a controversial Pd^{II}/Pd^{IV} cycle has been suggested as a potential catalytic mechanism.[28] However, a Pd^{IV} species has never been detected to date in one of these systems. Recently, we and Bergbreiter et al. studied the stability of supported SCS pincer complexes independently.[57,58,74] Both groups demonstrated that these complexes leach unidentified Pd(0) species into solution that are catalytically active. Furthermore, no catalytic activity could be attributed to any intact pincer species. In view of these results, we decided to investigate palladated PCP complexes that are reported in the literature to be significantly more stable.[75−77] The literature concerning these species in the Heck reaction is somewhat muddled. Eberhard[69] has demonstrated that palladated PCP pincer complexes with oxygen atoms in place of carbons in the arms are not stable during Heck catalysis (Figure 2), Frech[78] has shown recently that the palladated pincer ligand could be reduced by sodium to form a bimetallic complex, whereas there are other reports where immobilized PCP pincers are reported as "recyclable catalysts".[67]

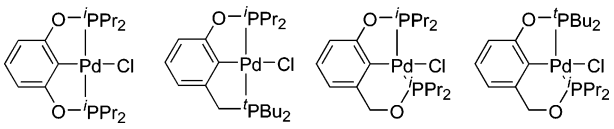


Figure 2. Pincer ligands studied by Eberhard.[69]

We have prepared the small-molecule Pd(II) PCP pincer (**1**) and compared its performance in the Heck reaction with that of Pd(II) PCP complexes tethered to a variety of supports ranging from soluble polymers (**2** and **3**) to nanoporous silica, SBA-15 (**4**) (Figure 3). Silica-supported catalysts allowed for easy removal of the catalyst from the reaction mixture, while soluble polymer supported catalysts allowed us to study the reactivity of the catalytic species in a homogeneous solution. In this work, we report the synthesis of these supported pincer complexes and a detailed study of their stability under Heck catalysis conditions. Using a variety of techniques such as in situ NMR and poisoning studies, our data suggest that, in all cases studied, the pincer species decompose, releasing Pd(0), which is the catalytically active species. Finally, in situ NMR and in situ X-ray absorption spectroscopy (XAS) are used to explore the stability of the complexes, while mass spectroscopy and computational experiments are used to explore the first steps of the decomposition pathway.

(45) Rahimm, E. H.; Kamounah, F. S.; Frederiksen, J.; Christensen, J. B. *Nano Lett.* **2001**, *1*, 499.
(46) Yeung, L. K.; Crooks, R. M. *Nano Lett.* **2001**, *1*, 14.
(47) Sablong, R.; Schlotterback, U.; Vogt, D.; Mecking, S. *Adv. Synth. Catal.* **2003**, *345*, 333.
(48) Heidenreich, R. G.; Krauter, J. G. E.; Pietsch, J.; Kohler, K. *J. Mol. Catal. A* **2002**, *182−183*, 499.
(49) Kohler, K.; Heidenreich, R. G.; Krauter, J. G. E.; Pietsch, J. *Chem. Eur. J.* **2002**, *8*, 622.
(50) Kohler, K.; Wagner, M.; Djakovitch, L. *Catal. Today* **2001**, *66*, 101.
(51) Nejjar, A.; Pinel, C.; Djakovitch, L. *Adv. Synth. Catal.* **2003**, *345*, 612.
(52) Zhao, F.; Bhanage, B. M.; Shirai, M.; Arai, M. *Chem. Eur. J.* **2000**, *6*, 843.
(53) Zhao, F.; Murakami, K.; Masahiko, A. *J. Catal.* **2000**, *194*, 479.
(54) Bergbreiter, D. E.; Osburn, P. L.; Liu, Y. S. *J. Am. Chem. Soc.* **1999**, *121*, 9531.
(55) Bhanage, B. M.; Fujita, S. I.; Arai, M. *J. Organomet. Chem.* **2003**, *687*, 211.
(56) Uozumi, Y.; Kimura, T. *Synlett* **2002**, *12*, 2045.
(57) Yu, K.; Sommer, W.; Weck, M.; Jones, C. W. *Adv. Synth. Catal.* **2005**, *347,* 161.
(58) Yu, K.; Sommer, W.; Weck, M.; Jones, C. W. *J. Catal.* **2004**, *226*, 101.
(59) Deprele, S.; Montchamp, J. L. *Org. Lett.* **2004**, *6*, 3805.
(60) McNamara, C. A.; Dixon, M. J.; Bradley, M. *Chem. Rev.* **2002**, *102*, 3275.
(61) Saluzzo, C.; Lemaire, M. *Adv. Synth. Catal.* **2002**, *344*, 915.
(62) Bergbreiter, D. E.; Osburn, P. L.; Wilson, A.; Sink, E. M. *J. Am. Chem. Soc.* **2000**, *122*, 9058.
(63) Gimenez, R.; Swager, T. M. *J. Mol. Catal. A* **2001**, *166*, 265.
(64) Koh, J. H.; Gagné, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 3459.
(65) Mas-Marza, E.; Segarra, A. M.; Claver, C.; Peris, E.; Fernandez, E. *Tetrahedron Lett.* **2003**, *44*, 6595.
(66) Weissberg, A.; Portnoy, M. *Chem. Commun.* **2003**, 1538.
(67) Chanthateyanonth, R.; Alper, H. *Adv. Synth. Catal.* **2004**, *346*, 1375.
(68) Karlen, T.; Dani, P.; Grove, D. M.; Steenwinkel, P.; van Koten, G. *Organometallics* **1996**, *15*, 5687.
(69) Eberhard, M. R. *Org. Lett.* **2004**, *6*, 2125.
(70) Morales-Morales, D.; Redon, R.; Yung, C.; Jensen, C. M. *Inorg. Chim. Acta* **2004**, *357*, 2953.
(71) Pollino, J. M.; Weck, M. *Org. Lett.* **2002**, *4*, 753.
(72) Pollino, J. M.; Weck, M. *Synthesis* **2002**, *9*, 1277.
(73) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837.
(74) Bergbreiter, D. E.; Osburn, P. L.; Frels, J. *Adv. Synth. Catal.* **2005**, *347*, 172.
(75) Miyazaki, F.; Yamaguchi, K.; Shibasaki, M. *Tetrahedron Lett.* **1999**, *40*, 7379.
(76) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687.
(77) Morales-Morales, D.; Grause, C.; Kasaoka, K.; Redon, R.; Cramer, R. E.; Jensen, C. M. *Inorg. Chim. Acta* **2000**, *958*, 300.
(78) Frech, C. M.; Shimon, L. J. W.; Milstein, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 1709.

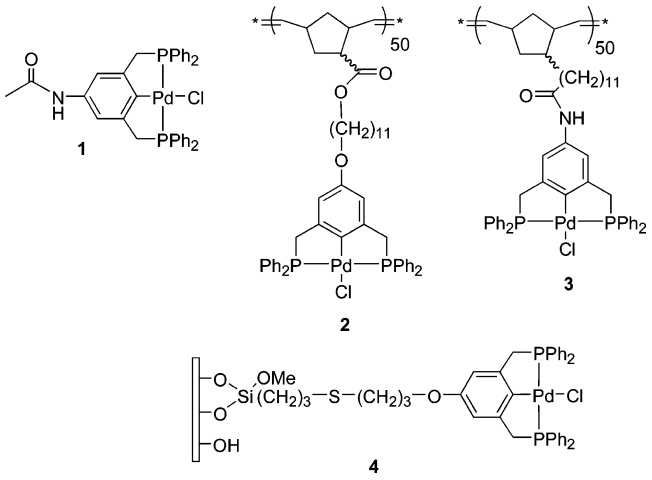


Figure 3. Immobilized palladated pincer complexes evaluated in this work.

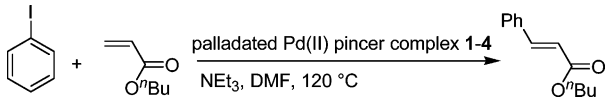


Figure 4. Heck reaction conditions.

Results and Discussion

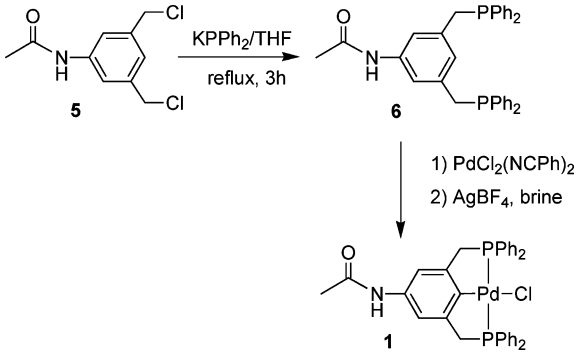
We conducted our investigation using four different catalysts with similar structures. Complex **1** was used as the standard for all catalytic reactions, for comparison with the supported systems. The polymer-supported catalysts **2** and **3** were synthesized to study the effect of the linker attachment on the catalytic activity. It has been suggested in the literature that ether derivatives of pincer complexes are less stable than their amide counterparts.[54] Therefore, two polymeric catalysts that are similar except for the heteroatom functionality that attaches the pincer complex to the support were prepared. For **2**, the catalyst was attached to the polymer backbone via an ether linkage, while in the case of **3**, an amide linkage was employed. Both polymers are highly soluble under reaction conditions, allowing a close comparison with **1**. The silica-supported catalyst **4** was synthesized to study the influence of a heterogeneous reaction mixture on the catalysis and to compare the catalytic activity of a solid-supported system to the soluble polymer catalysts and the small-molecule analogue.

The standard Heck reaction conditions are outlined in Figure 4. The catalysis was carried out using 1.5 equiv of distilled triethylamine, 1 equiv of iodobenzene, and 1.25 equiv of *n*-butyl acrylate in DMF at 120 °C. The catalyst loading was 10 mol % for the polymer-supported pincer and 0.3 mol % for the SBA-15-supported pincer.

The synthesis of **1** was carried out by reacting **5** (synthesized according to literature procedures[9]) with potassium diphenylphosphide in THF under reflux for 3 h to yield **6**, which was used without further purification. Compound **6** was then dissolved in a CH_2Cl_2/MeCN (1:2) mixture followed by the addition of the $PdCl_2(NCPh)_2$ and $AgBF_4$ to yield **1**, after purification, as a yellow solid (Scheme 1).

The use of **1** in Heck catalysis was investigated by monitoring the disappearance of iodobenzene via gas

Scheme 1. Synthesis of Palladium Chloride *N*-{3,5-Bis[(diphenylphosphanyl)methyl]phenyl}-acetamide (1)



chromatography (GC). We observed quantitative conversion using **1** as catalyst within 20 min (Figure 5). To examine the catalytic behavior in more detail, poisoning studies were carried out. It has been demonstrated that highly cross-linked poly(vinylpyridine) (PVPy) traps soluble Pd species by coordinating to the metal center and removing it from solution, while leaving support-tethered Pd species untouched.[56,57,79] For the poisoning test, 300 equiv of PVPy was added to the catalytic reaction, resulting in less than 2% conversion of iodobenzene after 3 h. A second poisoning test was carried out by adding mercury. Hg(0) is known to react with Pd(0), forming an amalgamate, thereby quenching the activity of the leached palladium.[79−81] When 100 equiv of mercury was added to the catalytic reaction, again, less than 2% conversion of iodobenzene was observed after 3 h. These results clearly suggest that **1** decomposes under the reaction conditions.[57,58,74]

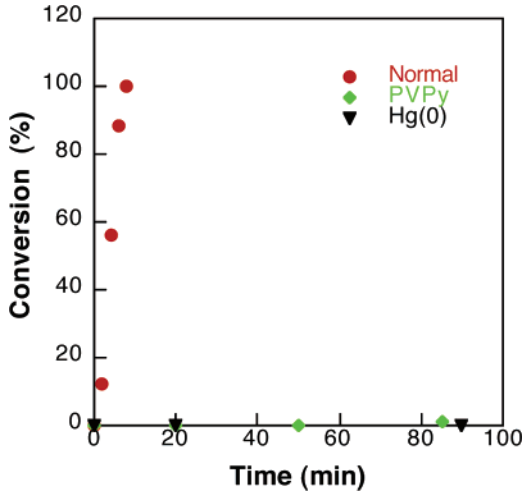
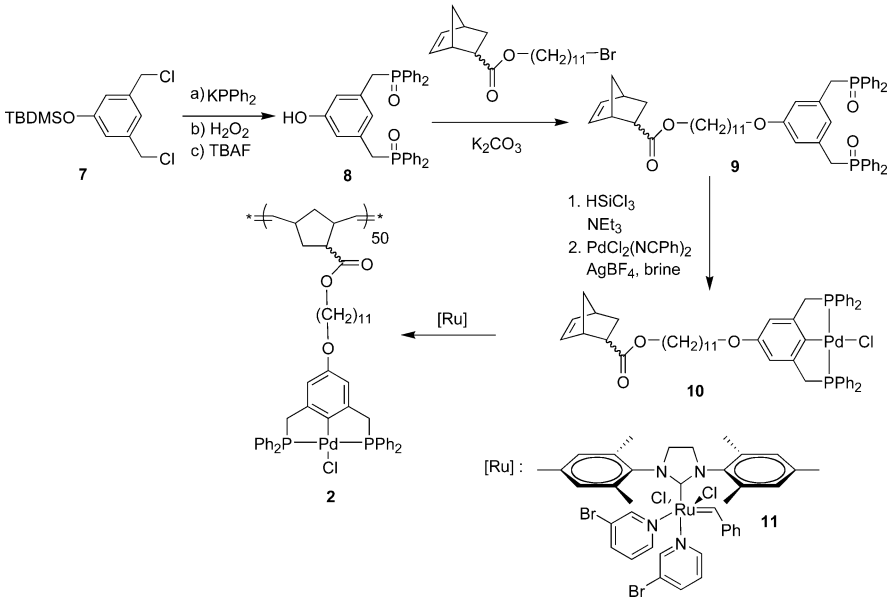


Figure 5. Conversion vs time for Heck coupling using **1**.

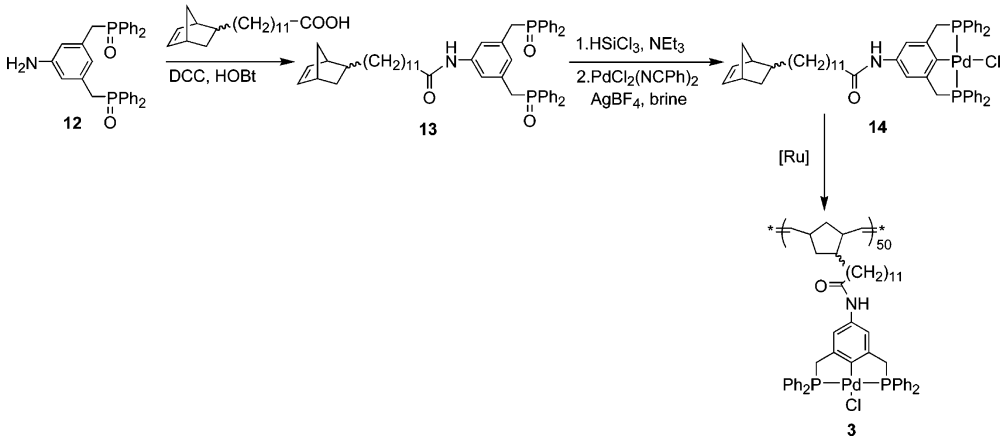
The synthesis of polymer **2** was accomplished by adding potassium diphenylphosphide to **7**, which was synthesized using a literature procedure,[9] followed by the oxidation of the phosphorus using an aqueous solution of 10% H_2O_2. The *tert*-butyldimethylsilyl group was then removed using TBAF to yield **8** as a white

(79) Klingelhöfer, S.; Heitz, W.; Oestreich, S.; Förster, S.; Antonietti, M. *J. Am. Chem. Soc.* **1997**, *119*, 10116.
(80) Paal, C.; Hartmann, W. *Chem. Ber.* **1918**, *51*, 711.
(81) Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J. P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819.

Scheme 2. Synthesis of Polymer 2



Scheme 3. Synthesis of Polymer 3



solid, which was reacted with the cyclo[2.2.1]hept-5-ene-2-carboxylic acid 11-bromoundecyl ester using potassium carbonate in DMF to yield a brown oil. The oil was immediately reacted with trichlorosilane and triethylamine in xylenes to deprotect the phosphines. The deprotected pincer was then reacted with $PdCl_2(NCPh)_2$ and $AgBF_4$ to yield monomer **10** as an orange solid. The monomer was polymerized using the third-generation Grubbs catalyst at room temperature under air (Scheme 2).[83] Quantitative conversion was obtained in 20 min.

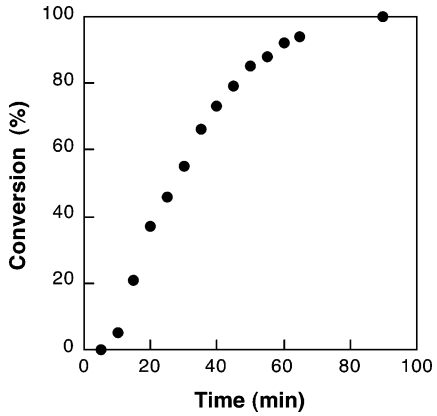


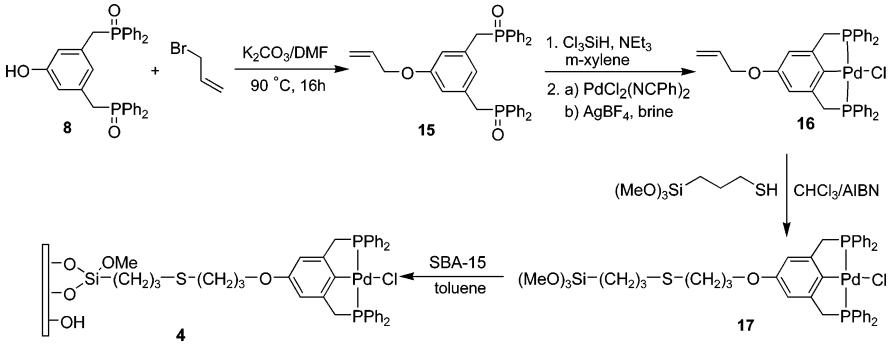
Figure 6. Conversion vs time for Heck coupling using **2**.

Again, the use of polymer **2** under Heck conditions was measured using GC by following the disappearance of iodobenzene (Figure 6). We observed quantitative conversion within 90 min. In analogy to the experiments outlined above for **1**, poisoning studies were carried out. The addition of 300 equiv of PVPy resulted in the retardation of the reaction with only 1% conversion observed after 24 h. Furthermore, the addition of 100 equiv of mercury to the Heck reaction mixture yielded similar results. Again, these experiments suggest that the active species for the Heck reaction is not a well-defined palladium species but a leached Pd moiety that contains Pd(0) in the catalytic cycle.

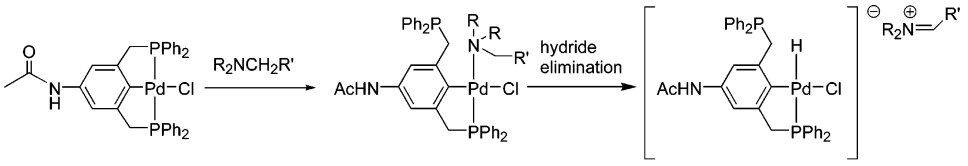
Polymer **3** was synthesized by starting with the coupling of complex **12** and 12-bicyclo[2.2.1]hept-5-en-2-yldodecanoic acid using dicyclohexylcarbodiimide and 1-hydoxybenzotriazole to yield **13**. Reduction of the phosphorus using trichlorosilane and triethylamine in xylenes, followed by the addition of $PdCl_2(NCPh)_2$ and $AgBF_4$, yielded monomer **14** (Scheme 3). The monomer was polymerized using the third-generation Grubbs catalyst **11** in a 50:1 monomer-to-catalyst ratio.

(82) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A* **2003**, *198*, 317.
(83) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035.

Scheme 4. Synthesis of Silica-Tethered Pincer Complex 4



Scheme 5. Proposed Initial Steps of the Decomposition of the Palladated Pincer Complex



R_2NCH_2R' = NEt_3 (for all catalysis experiments and computational studies)
$N(Cyclohexyl)_2Me$ (for mass spectroscopy study)

The same reactivity experiments as outlined above for **1** and **2** were carried out. While quantitative conversion without the addition of poison was observed within 60 min (Figure 7), the two poisoning tests using 300 equiv of PVPy and 100 equiv of mercury resulted in the near-total quenching of the catalytic reaction. Both reactions yielded less than 1% conversion after 24 h. These results showed that the leaching of the palladium is independent of the tether group of the immobilized pincer complex and correlate well with the results for the other experiments discussed above.

To synthesize the silica-supported complex **4**, compound **8** was reacted with allyl bromide, followed by the reduction of the phosphorus using trichlorosilane and triethylamine in xylenes. Addition of $PdCl_2(NCPh)_2$ and $AgBF_4$ yielded **16** as a yellow powder. Complex **16** was then reacted with (3-mercaptopropyl)trimethoxysilane and AIBN in dry chloroform to yield **17**. Complex **17** was stirred with SBA-15 silica in toluene to yield the supported pincer complex **4** (Scheme 4).

Using **4** as Heck catalyst resulted in the quantitative conversion of iodobenzene within 2 h (Figure 8). The PVPy and mercury leaching tests were carried out, and no conversions were observed in the presence of either poison.

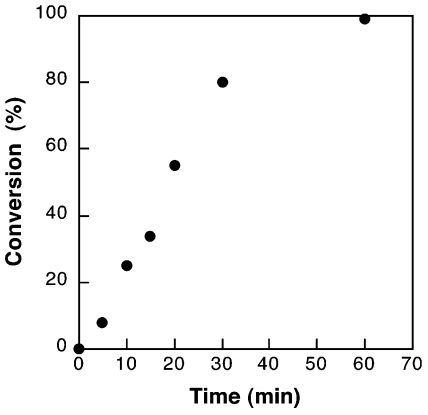


Figure 7. Conversion vs time for Heck coupling using **3**.

These reactivity experiments clearly demonstrate that palladated PCP complexes decompose under the reaction conditions studied. Furthermore, the decomposition is independent of the support or the linker attachment. While small differences in the kinetics of the reactions are observed for the different supports, poisoning studies for all systems studied demonstrate that no catalytic activity stems from a support-tethered Pd(II) species; rather, leached Pd species are the active moieties. These results are analogous to those of our recently reported study on supported SCS pincer complexes, clearly demonstrating that the added stability of the PCP ligand system is not enough to prevent decomposition.[57,58]

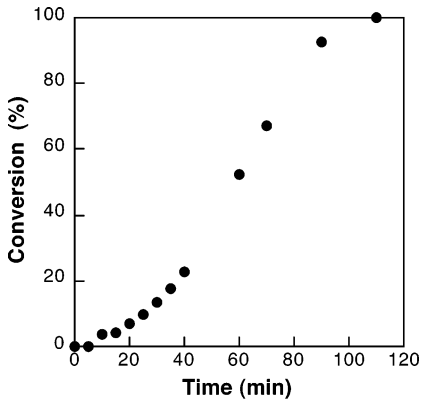


Figure 8. Conversion vs time for Heck coupling using **4**.

Investigations into the Decomposition Pathway. A variety of decomposition pathways of these complexes during reaction conditions are imaginable. The most likely decomposition pathway of palladacycles starts with the exchange of one ligand of the pincer ligand (arm off) by the nitrogen-containing base. As outlined in the literature, the high strain of palladated pincer complexes as a result of their distorted-square-planar configuration makes them likely to dechelate under appropriate reaction conditions, thereby relieving the strain.[30] After base or solvent coordination, the resulting

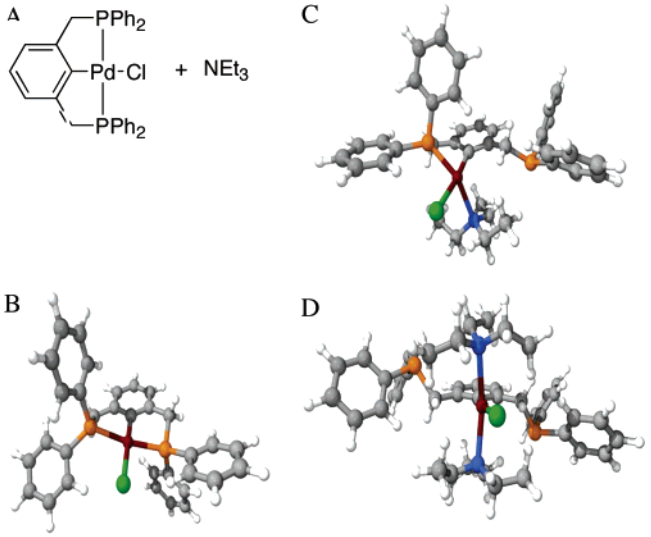


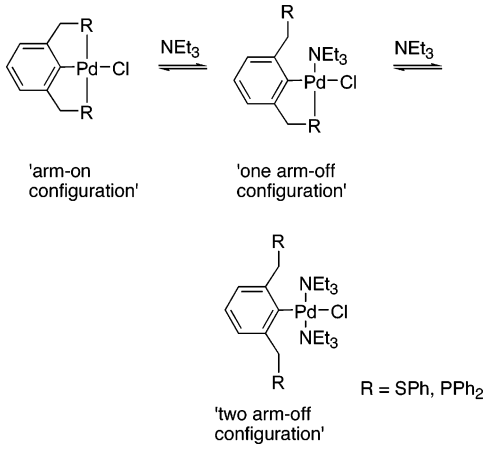
Figure 9. Optimized structures of the calculated exchange pathway of phosphine by a triethylamine base of palladated pincer complexes: (A) Chemdraw representation of structures used in calculation; (B) fully intact complex; (C) removal of one phosphine and addition of the amine base; (D) exchange of the second phosphine by another amine base.

complex resembles a half-pincer complex. Hartwig and Louie have shown that half-pincer complexes containing an amine base as ligand are able to undergo β-hydrogen elimination, a common reaction pathway of palladium amides with β-hydrogens, resulting in a palladium hydride species.[27,30] We propose that the second step of the catalyst decomposition may follow the same pathway of β-hydrogen elimination, as outlined in Scheme 5, creating a charged palladium hydride species with the iminium ion as a counterion.

To investigate this proposed decomposition pathway, we carried out a variety of in situ low- and high-temperature NMR experiments and mass spectroscopy experiments, supported by electronic structure computations and XAS studies. The hypothesis that the palladated PCP pincer is in an equilibrium between an arm-on configuration, i.e. a phosphine, bound to the palladium via a dative bond, and an open coordination site as a result of the breakage of this dative bond (arm-off configuration) is essential to most potential decomposition mechanisms.[41,84,85] Therefore, initially we concentrated our research efforts to evaluate this hypothesis.

Electronic structure computations were carried out to establish the energetics of the replacement of the phosphine ligands by the amine base (Scheme 6). Optimized geometries (computed using the BP86 density functional method with a LAV3P/6-31G* basis; see below) are presented in Figure 9, and relative energies for the PCP and SCS systems are depicted in Figure 10. For reasons discussed below, the reported energies include only zero-point vibrational and solvation energy corrections. These calculations suggested that the "one-arm-off configuration" of palladated PCP complexes requires about 21 kcal/mol in the presence of a coordinating ligand such as the amine, an uphill reaction

Scheme 6. Computational Explored Ligand Exchange Mechanism



energy that could be overcome at high temperatures such as the reaction conditions (preliminary computations for the simpler SCS system indicate that the transition state for this associative displacement is only an additional 2−3 kcal/mol beyond the reaction energy). Removal of the second arm and replacing it with another ligand such as the solvent and/or the amine base is estimated to cost an additional 13 kcal/mol relative to the "one-arm-off configuration". After the initial removal of the first arm, the coordination sphere around the palladium is a highly distorted square planar one (Figure 9C), which is highly unfavorable. However, this can be overcome during the second phosphine removal that converts the metal complex back into a square-planar configuration (Figure 9D), which explains why the second ligand exchange is less unfavorable than the first one. On the basis of these calculations, we hypothesize that the high temperatures during the reaction conditions allow the phosphorus ligands to come off of the metal center and to be replaced by other ligands such as the amine base. To support this hypothesis, we carried out a series of ^{31}P NMR experiments using **1**.

If an arm-on/arm-off equilibrium took place in the absence of additional ligands, one might expect to freeze out these states, leading to two distinct ^{31}P NMR signals at low temperatures that should coalesce at higher temperatures. However, only a single phosphorus signal at 15.7 ppm at −70 °C was detected in a variety of solvents, clearly demonstrating the stability of the Pd−P bonds at low temperatures. To investigate the role of the reactants toward the decomposition of the catalyst, we carried out a series of NMR experiments with triethylamine and/or iodobenzene present in the catalyst solution. Initially, equimolar ratios of **1**, triethylamine, and iodobenzene were observed in situ at 120 °C in DMF. Over a period of several hours, only one phosphorus signal was detected. However, addition of 3 equiv more of triethylamine resulted in the formation of two new signals in the phosphorus NMR at 7.7 and −4.2 ppm. Furthermore, palladium black formation was visible, confirming the decomposition of the metal complex. While we were not able to assign these two new signals in the NMR unequivocally, they are clearly indicative of a new phosphorus species.

To further investigate if both iodobenzene and triethylamine are needed for decomposition or if the

(84) Poverenov, E.; Gandelman, M.; Shimon, L. J. W.; Rozenberg, H.; Ben-David, Y.; Milstein, D. *Chem. Eur. J.* **2004**, *10*, 4673.
(85) Bassetti, M.; Capone, A.; Salamone, M. *Organometallics* **2004**, *23*, 247.

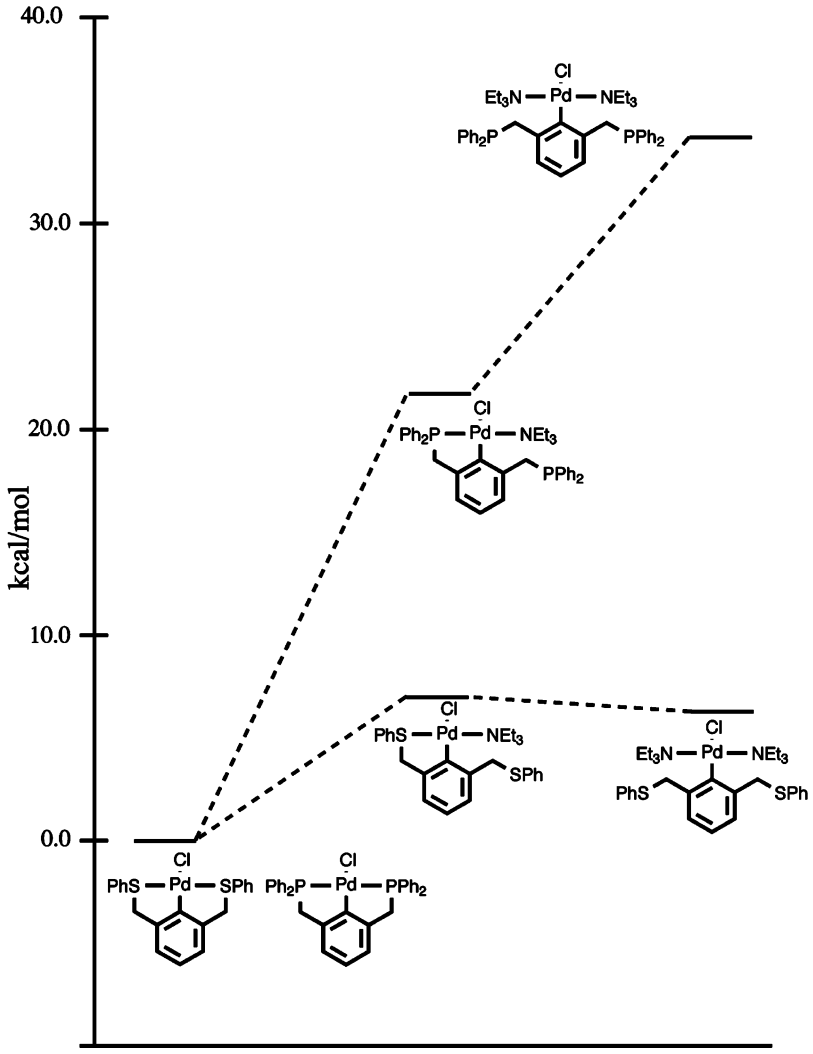


Figure 10. Free energy diagram of the relevant minima for the initial steps of the proposed decomposition pathway computed at the BP86/LAV3P/6-31G* level of theory.

decomposition pathway might follow the one outlined in Scheme 5, i.e. only the amine base is needed, additional experiments were carried out to verify the role of each reactant. Addition of iodobenzene to the metal complex at 120 °C in DMF resulted in no changes in the NMR over a period of 24 h and no palladium black formation was observed, even when 20 equiv of iodobenzene was added. In contrast, the addition of 7 equiv of triethylamine without the presence of an aryliodide species resulted in the formation of a new signal, 19 ppm upfield from the original signal. These results suggest that triethylamine plays an essential role in the decomposition of the palladium/pincer complex.

Theoretical investigations of the second step of the proposed decomposition pathway, the β-hydride elimination, would be very challenging and are beyond the scope of the present study. Nevertheless, initial computations of subsequent steps for the simpler SCS system indicate that hydride transfer to the aromatic carbon and concomitant cleavage of the carbon−palladium bond is energetically downhill by at least 20 kcal/mol relative to the intact palladacycle. To probe the proposed β-hydride elimination step of the decomposition pathway, we carried out a series of mass spectroscopy experiments. On the basis of the work of Hartwig and Louie,[30] the amine base will exist, after β-hydride elimination, as an iminium ion that can be hydrolyzed to yield a secondary amine. The presence of this secondary amine can be easily characterized using mass spectroscopy. Therefore, characterization of a reaction mixture using mass spectroscopy (ESI) is a facile method to evaluate the proposed β-hydride elimination decomposition step. For ease of characterization, dicyclohexylmethylamine was employed in the mass spectroscopy studies instead of the otherwise used triethylamine. The experiments were carried out by dissolving a mixture of catalyst **1** and dicyclohexylmethyl amine in DMF and heating it at 120 °C for several hours. Every 1 h, an aliquot was taken from the reaction mixture and analyzed by mass spectroscopy. All aliquots analyzed via mass spectroscopy (ESI) showed molecular ion signals at 182.3. This molecular ion signal is indicative of the presence of dicyclohexylamine. This result supports the hypothesis that the decomposition pathway goes through a β-hydrogen elimination step before the palladium(0) leaches out.

In two recent papers, we communicated also the decomposition of palladated SCS pincer complexes during Heck catalysis.[57,58] To investigate whether these palladated SCS pincer catalysts also follow the decomposition pathway identified for their PCP analogues, we carried out XAS experiments and computational studies.

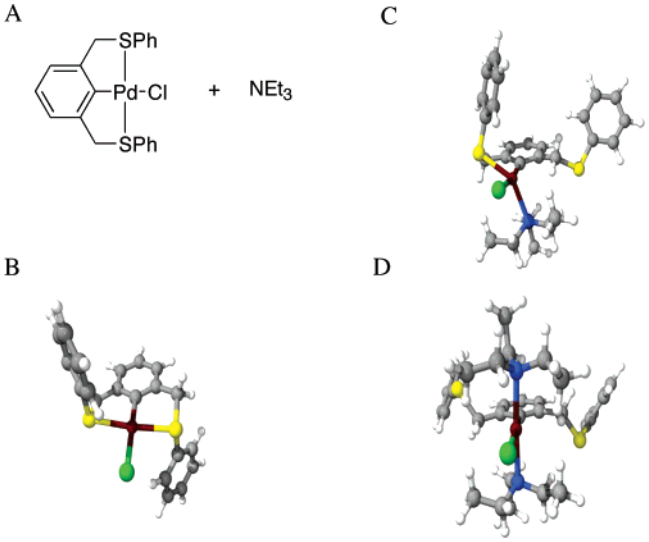


Figure 11. Optimized structures of the calculated exchange pathway of sulfur by a trimethylamine base of palladated pincer complexes: (A) Chemdraw representation of structures used in calculation; (B) fully intact complex; (C) removal of one sulfur and addition of the amine base; (D) exchange of the second sulfur by another amine base.

Table 1. Relative BP86/LAV3P/6-31G* Energies in kcal mol^{-1} for Optimized Structures[a]

compd	ΔE_{elec} (kcal mol^{-1})	$\Delta E_{elec} + \Delta E_{solv}$ (kcal mol^{-1})	$\Delta E_{elec} + \Delta E_{solv} +$ ΔZPVE (kcal mol^{-1})
PCP−Pd−Cl	0.0	0.0	0.0
PC_P−Pd(Cl)(NEt_3)	17.0	19.9	21.1
$_PC_P$−Pd(Cl)(NEt_3)$_2$	25.5	31.0	34.1
SCS−Pd−Cl	0.0	0.0	0.0
SC_S−Pd(Cl)(NEt_3)	2.6	5.6	7.0
$_SC_S$−Pd(Cl)(NEt_3)$_2$	−4.2	3.2	6.4

[a] Subscript letters denote noncoordinated atoms.

The electronic structure computations of the palladated SCS pincer complex (optimized structures are outlined in Figure 11; relative energies shown in Table 1) suggested that the one-arm-off configuration is only 7.0 kcal/mol higher in energy than the palladated SCS pincer complex in the presence of an amine base. Furthermore, removal of the second arm is calculated to be downhill relative to the one-arm-off configuration by 0.6 kcal/mol. These calculations are supported by the observation of palladium black formation in the reaction vessel when adding only 1 equiv of triethylamine to a poly(norbornene)-supported SCS Pd(II) pincer complex. This is in stark contrast to the required 7 equiv of triethylamine required for the visible decomposition of the PCP analogue **1** and can be explained by the known lesser stability of SCS complexes.[54,86]

The in situ XAS data on both the polymeric and silica-immobilized palladated SCS pincer complexes, under Heck reaction conditions, show the formation of palladium iodide species, while no metallic palladium was found under the reaction conditions (for a detailed description of the XAS data, see the Supporting Information). It has been reported in the literature that soluble palladium species are stored as palladium halides, such as the bridged $[Pd_2I_6]^{2-}$ anion.[106] Our XAS study clearly supports these reports. It is important to note that the majority of our computational and NMR studies, in contrast to all XAS experiments, were carried out in the absence of an aryl iodide. When no aryl iodide was present during the NMR experiments, palladium black formation was observed, suggesting the formation of metallic palladium. However, when NMR experiments were carried out in the presence of aryl iodide, palladium black formation was significantly less pronounced, suggesting the storage of the majority of palladium in a form other than Pd(0). On the basis of our XAS results, palladium iodide species are therefore the likely storage species. Overall, the XAS results clearly demonstrate that the SCS pincer complexes are altered under reaction conditions, thereby substantiating the NMR and computational studies, while suggesting that the most abundant soluble palladium species under reaction conditions are palladium iodides.

When the experimental and computational data on the decomposition of palladated PCP and SCS pincer complexes are combined, it is obvious that the amine base plays the key role in the decomposition pathway. On the basis of the data outlined above, we suggest that catalyst decomposition could occur through exchange of a phosphorus or sulfur ligand (one arm of the pincer ligand) with triethylamine, followed by a β-hydrogen elimination of the base and a rapid second ligand exchange, thereby changing the pincer ligands from tridentate ligands to monodentate ones. Furthermore, our calculations follow the reported trend of PCP-based complexes being significantly more stable than their SCS counterparts.[86] However, at the commonly employed reaction temperatures, both complexes decompose, thereby releasing soluble palladium species. Although the XAS studies clearly indicate that the primary Pd species in solution is a Pd(II) moiety, the Hg(0) poisoning studies unequivocally show that the catalytic cycle contains a Pd(0) intermediate, as Hg(0) addition quenches essentially all activity. As noted in our earlier studies, however, the nature of the true zerovalent catalyst cannot be conclusively determined with the data here (Pd(0) colloid[40] or molecular Pd(0) species[87−89]), as it is expected that Hg(0) would poison either type of species.[90] Nonetheless, a number of observations imply

(86) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759.

(87) Cassol, C. C.; Umpierre, A. P.; Machado, G.; Wolke, S. I.; Dupont, J. *J. Am. Chem. Soc.* **2005**, *127*, 3298.

(88) de Vries, A. H. M.; Mulders, J. M. C. A.; Mommers, J. H. M.; Henderickx, H. J. W.; de Vries, J. G. *Org. Lett.* **2003**, *5*, 3285.

(89) Reetz, M. T.; De Vries, J. G. *Chem. Commun.* **2004**, 1559.

(90) It has been argued that precursor complexes such as palladacycles decompose to give active Pd(0) nanoparticles. This is because previous Hg test results where Hg(0) poisons catalysis have been interpreted as proof for catalysis by heterogeneous catalysts (colloids in this case). We hypothesize here that Hg(0) will also extinguish catalysis by molecular Pd(0) "naked" species[87−89] that are not protected by strongly bound ligands. Unfortunately, at times, the historic literature is interpreted as saying that the Hg test distinguishes between homogeneous and heterogeneous catalysis. This is often the case in the context of the original studies. Indeed, the historic literature[104,105] with the Hg(0) test focuses on hydrogenation reactions with metal complexes in elevated formal oxidation states bound by protective ligands. Certainly, these catalysts are not affected by Hg(0), as they are not M(0) species and they are protected by strong ligands. We have also shown that Pd(II) pincers are also unaffected by Hg(0) when carrying out stoichiometric reactions where the ligand remains intact and the complex is in a Pd(II) state.[57] However, we hypothesize that "naked" molecular Pd(0) species[87−89] that have been postulated to be the true active catalytic species in some cases are examples of homogeneous catalysts that should be affected by Hg(0), as a consequence of their lack of protecting strong ligands and their M(0) state.

that molecular species could be important in the Heck reaction, including the observed reactivity and the high concentration of $[Pd_2I_6]^{2-}$ species in ligand-free Pd catalysts,[89] our XAS observations here, kinetic and other data presented in the literature,[87,88] and the fact that enantioselective Heck reactions are possible with chiral ligands.[91] None of these observations would be expected if Pd(0) colloids were the primary active species.

Conclusions

We have demonstrated using a variety of leaching experiments and kinetic studies that palladated PCP pincer complexes (homogeneous species as well as complexes immobilized on soluble and insoluble supports), which have been identified in the literature as stable entities,[67,68] decompose under Heck reaction conditions. Through the employment of computational methods, X-ray absorption spectroscopy, mass spectroscopy, and in situ NMR spectroscopy, we have proposed the initial steps of the decomposition pathway of these PCP as well as SCS pincer complexes. It is important to note that our conclusions are limited to the organic bases used in this paper. Heck catalysis using palladated pincer ligands have also been carried out using inorganic bases such as K_2CO_3. We do not suggest a decomposition pathway when inorganic bases are used. The data outlined in this contribution combined with recent reports from the literature[57,58,69,74] call into question whether any palladated pincer complexes that have a palladium(II) metal center are truly stable under the reaction conditions for carbon−carbon bond formations such as Heck and Suzuki couplings. Indeed, others have recently observed the decomposition of Pd(II) PCP pincers in related coupling reactions.[107] Rather, these species should be referred to as precatalysts and supported analogues as recyclable precatalyst sources.

Experimental Section

General Considerations. All reactions with air- and moisture-sensitive compounds were carried out under a dry nitrogen/argon atmosphere using an MBraun UniLab 2000 drybox and/or standard Schlenk line techniques. DMF, *n*-butyl acrylate, and NEt_3 were distilled over calcium hydride. 5-Aminoisophthalic acid dimethyl ester, poly(4-vinylpyridine), (3-isocyanatopropyl)triethoxysilane, and all bases were obtained from commercial sources and generally used without further purification. Gas chromatographic analyses were performed on a Shimadzu GC 14-A gas chromatograph equipped with a flame-ionization detector with an HP-5 column (length 30 m, inner diameter 0.25 mm, and film thickness 0.25 um). The temperature program for GC analysis was as follows: heating from 50 to 140 °C at 30 °C/min and heating from 140 to 300 °C at 40 °C/min under constant pressure with inlet and detector temperatures kept constant at 330 °C. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian Mercury VX instrument. ^{31}P NMR (162 MHz) spectra were recorded on a Bruker AMX 400 MHz instrument using H_3PO_4 as a calibration standard. All spectra were referenced to residual proton solvent. Mass spectral analyses were provided by the Georgia Tech MassSpectrometry Facility using a VG-70se spectrometer. Gel-permeation chromatography analyses were carried out using a Waters 1525 binary pump coupled to a Waters 2414 refractive index detector. The GPC was calibrated using poly(styrene) standards on a Styragel HR 4 and HR 5E column set with CH_2Cl_2 as an eluent. FT-Raman spectra were obtained on a Bruker FRA-106 instrument. At least 128 scans were collected for each spectrum, with a resolution of 2−4 cm^{-1}. Elemental analyses were carried out by either Atlantic Microlabs, Norcross, GA (CHN analyses), or Galbraith Laboratories, Inc., TN (determination of the palladium loadings of the silica precatalysts). SBA-15 (100 Å pore size) was synthesized following a literature method.[92] The as-prepared material was calcined using the following temperature program: (1) increasing the temperature (1.2 °C/min) to 200 °C, (2) heating at 200 °C for 1 h, (3) increasing at 1.2 °C/min to 550 °C, and (4) holding at 550 °C for 6 h. Prior to functionalization, the SBA-15 was dried under vacuum at room temperature overnight and then at 120 °C/min for 3 h and stored in a drybox.

Computations. All of the calculations presented in this work used the pseudospectral implementation[93] of density functional theory within Jaguar.[94] All calculations employed the nonlocal gradient corrected exchange functional of Becke[95] and the correlation functional of Perdew,[96] the combination commonly referred to as BP86. The relativistic effective core potentials of Hay and Wadt, LAV3P, were used for Cl, P, and Pd atoms.[97,98] A 6-31G* basis set was used for first- and second-row atoms.[99] Harmonic vibrational frequencies were computed for each of the stationary points to verify the nature of the optimized structures. Zero-point vibrational energy corrections were computed from the harmonic frequencies, scaled by 1.0108 as suggested in the literature.[100] Due to the difficulty in computing accurately the changes in translational and rotational entropy upon coordination[101] and the presence of large-amplitude vibrations in these systems, which would not be accurately modeled in the harmonic oscillator approximations, corrections for finite temperature were not included. Implicit solvent effects were incorporated at the gas-phase optimized structures using the self-consistent reaction field approach as implemented in Jaguar.[102] The density of DMF at 120 °C was taken to be 0.8521 g/cm^3, and the dielectric constant was taken to be 24.7.[103] The SCRF calculations, employing the same functional and basis set used in the rest of the work, were used to determine energy corrections for each structure. The energies reported throughout this work, unless otherwise stated, include both the zero-point vibrational energy and the solvation energy corrections.

Synthesis of Palladium Chloride *N*-{3,5-Bis[(diphenylphosphanyl)methyl]phenyl}acetamide (1). Inside a nitrogen-filled drybox, $KPPh_2$ (4.1 mL, 0.5 M in THF) was slowly added to a THF solution (20 mL) of **5** (220 mg, 0.94 mmol). The reaction mixture was removed from the drybox, refluxed for 3 h, and cooled to room temperature. The solvent was removed under vacuum, and dry CH_2Cl_2 (50 mL) was added. The solution was washed with degassed H_2O (2 × 20 mL) and dried over anhydrous Na_2SO_4 and the solvent removed. The

(91) Shibasaki, M.; Vogl, E. M.; Ohshima, T. *Adv. Synth. Catal.* **2004**, *346*, 1533.
(92) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, J. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.
(93) Friesner, R. A. *Annu. Rev. Phys. Chem.* **1991**, *42*, 341.
(94) Jaguar 5.5; Schrodinger, LLC, Portland, OR, 1991−2003.
(95) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(96) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
(97) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.
(98) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
(99) Rassolov, V. A.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 1223.
(100) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.
(101) Amzel, L. M. *Proteins: Struct., Funct., Genet.* **1997**, *28*, 144.
(102) Tannor, D. J.; Marten, B.; Murphy, R.; Friesner, R. A.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1994**, *116*, 11875.
(103) Technical Leaflet M5351 e; BASF, NJ, 2000.
(104) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855.
(105) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc* **1980**, 102, 6713.
(106) Evans, J.; O'Neill, L.; Kambhampati, V. L.; Rayner, G.; Turin, S.; Genge, A.; Dent, A. J.; Neisius, T. *Dalton* **2002**, 2207.
(107) Olsson, D.; Nilsson, P.; El Masnoury, M.; Wendt, O. F. *Dalton* **2005**, 1924.

crude product was redissolved in 15 mL of CH_2Cl_2/CH_3CN (v/v 1:2), and $PdCl_2(NCPh)_2$ (320 mg, 0.83 mmol) was added. The reaction mixture was stirred at room temperature for 30 min, followed by the addition of $AgBF_4$ (485 mg, 2.49 mmol). After it was stirred for an additional 30 min, the mixture was diluted with CH_2Cl_2 (250 mL) and stirred with a saturated brine solution (200 mL) for 5 h. The organic layer was then separated, dried over Na_2SO_4, and passed through a short silica gel column. Solvent removal and recrystallization from CH_2Cl_2/Et_2O yielded **1** as a yellow powder. Yield: 340 mg (61%). ^{1}H NMR (d_6-DMSO, 300 MHz): δ 9.86 (s, 1H), 8.21−7.77 (m, 10H), 7.48−7.37 (m, 10H, Ph), 7.28 (s, 2H), 4.09 (bs, 4H), 1.96 (s, 3H). Anal. Calcd for $C_{34}H_{30}ClNOP_2Pd$: C, 60.73; H, 4.50; N, 2.08. Found: C, 60.34; H, 4.32; N, 1.94.

Synthesis of Palladium Chloride Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 11-{3,5-bis[(diphenylphosphanyl)-methyl]phenoxy}undecyl Ester (10). Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 11-bromoundecyl ester (767 mg, 2.06 mmol) was slowly added over a period of 15 min to a stirred solution of **8** (1.08 g, 2.06 mmol) and potassium carbonate (571 mg, 4.1 mmol) in DMF. The mixture was heated to 90 °C and stirred for 12 h. The DMF was removed in vacuo, the crude product dissolved in methylene chloride (100 mL), and this solution washed with 1 N HCl (50 mL), sodium bicarbonate (50 mL), and brine (50 mL). The organic layers were dried over magnesium sulfate and the solvent removed under vacuum to yield **9** as a viscous brown oil, which was partially purified via column chromatography (eluent ethyl acetate followed by methanol) and then used without further purification. Compound **9** (1.37 g, 1.7 mmol) was dissolved in degassed *m*-xylenes (50 mL), and triethylamine (5.7 mL, 40.5 mmol) was slowly added, followed by the dropwise addition of trichlorosilane (4.1 mL, 40.5 mmol). The reaction mixture was heated to 120 °C for 10 h. After the mixture was cooled to room temperature, it was poured into a degassed solution of sodium hydroxide (500 mL). The product was then extracted from the aqueous reaction mixture with toluene (2 × 100 mL), the extract dried over magnesium sulfate, and the solvent removed under vacuum to yield a yellow oil. The oil was dissolved in CH_2Cl_2/CH_3CN (5 mL/10 mL), and $PdCl_2(NCPh)_2$ (652 mg, 1.7 mmol) was added. The solution was stirred for 30 min before the addition of $AgBF_4$ (823 mg, 4.2 mmol). The mixture turned yellow and was stirred for another 30 min, diluted with CH_2Cl_2 (200 mL), poured into a concentrated brine solution (500 mL), and stirred vigorously for 5 h. The organic layer was separated and dried over $MgSO_4$, and the solvent was removed under vacuum to yield an orange oil that was purified via column chromatography (1:1 ethyl acetate/hexanes) to give **2** as an orange solid. Yield: 62%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.91−7.83 (m, 10H), 7.52−7.34 (m, 12H), 6.7 (s, 4H), 6.08−5.88 (m, 2H), 4.23 (br s, 4H), 3.83 (t, 2H, J = 6.2 Hz), 3.20−3.13 (m, 1H), 3.00−2.99 (m, 1H), 2.94−2.82 (m, 4H), 2.22−2.13 (m, 1H), 1.92−1.82 (m, 2H), 1.78−1.64 (m, 4H), 1.63−1.50 (m, 4H), 1.42−1.31 (m, 5H), 1.32−1.20 (m, 28H). HRMS (ESI): *m/z* 885.2534. Anal. Calcd for $C_{51}H_{57}ClO_3P_2Pd$: C, 66.45; H, 6.23. Found: C, 66.82; H, 6.11.

Synthesis of Palladium Chloride 12-Bicyclo[2.2.1]hept-5-en-2-yldodecanoic Acid {3,5-Bis[(diphenylphosphanyl)-methyl]phenyl}amide (14). To a solution of 12-bicyclo[2.2.1]-hept-5-en-2-yldodecanoic acid (120 mg, 0.4 mmol) in CH_2Cl_2 were added 1-hydroxybenzotriazole (55 mg, 0.4 mmol) and dicyclohexylcarbodiimide (85 mg, 0.4 mmol) with a few drops of DMF. To the reaction mixture was added complex **12** (214 mg, 0.4 mmol), and this mixture was stirred for 12 h. The reaction mixture was then filtered through a small patch of silica and the solvent removed under vacuum. Without further purification, compound **13** was dissolved in degassed xylenes (50 mL) followed by the addition of triethylamine (0.56 mL, 4 mmol) and dropwise addition of trichlorosilanes (0.56 mL, 4 mmol). The reaction mixture was heated to 120 °C for 12 h, cooled to room temperature, and transferred into a glovebox, where it was poured into a degassed solution of sodium hydroxide (2 M, 50 mL). The product was then extracted from the aqueous reaction mixture with toluene (2 × 50 mL), dried over $MgSO_4$, and the solvent removed to yield an off-white oil, which was dissolved into CH_2Cl_2/CH_3CN (5 mL/10 mL) followed by the addition of $PdCl_2(NCPh)_2$ (154 mg, 0.4 mmol). The reaction mixture was stirred for 30 min before the addition of $AgBF_4$ (195 mg, 1 mmol). The mixture was stirred for another 30 min, diluted with CH_2Cl_2 (200 mL), poured into a saturated brine solution, and stirred for 12 h. The organic phase was then separated and dried over $MgSO_4$, and the solvent was removed to yield an orange oil that was purified via a chromatography column (1:1 ethyl acetate/hexanes). Yield: 34%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.92−7.84 (m, 10H, PPh_2), 7.51−7.34 (m, 12H), 6.4 (s, 4H), 6.06−5.89 (m, 2H), 4.37 (br s, 4H), 2.71 (s, 2H), 2.29−2.24 (t, J = 7.3 Hz, 2H), 1.95−1.75 (m, 1H), 1.324 (t, J = 6.1 Hz, 2H), 1.324−1.15 (br m, 19H), 1.08−1.00 (m, 1H), 0.92−0.83 (m, 1H), 0.51−0.45 (m, 1H).^{13}C NMR ($CDCl_3$, 300 MHz): δ 171.9, 158.0, 149.8, 148.8, 133.9, 133.9, 131.9, 133.8, 132.4, 132.3, 132.2, 131.5, 131.4, 129.9, 129.7, 129.6, 128.1, 127.9, 113.8, 51.3, 49.5, 45.3, 42.4, 38.7, 37.5, 34.7, 32.4, 29.9, 29.6, 29.5, 29.3, 28.6, 25.7. HRMS (ESI): *m/z* 905.3275. Anal. Calcd for $C_{51}H_{58}ClNOP_2Pd$: C, 67.70; H, 6.46; N, 1.55; found C, 67.52; H, 6.42; N, 1.67.

Synthesis of Palladium Chloride 1-(Allyloxy)-3,5-bis-[(diphenylphosphanyl)methyl]benzene (16). To a dry DMF (20 mL) solution of complex **8** (400 mg, 0.77 mmol) were added K_2CO_3 (370 mg, 2.68 mmol) and allyl bromide (0.2 mL, 2.31 mmol). The resulting mixture was heated at 90 °C for 20 h. After the mixture was cooled to room temperature, DMF was distilled off and the product was extracted with CH_2Cl_2 (2 × 50 mL) and the extract washed with H_2O (2 × 20 mL) and dried over anhydrous Na_2SO_4. Purification through a flash silica gel column afforded **15** as an off-white oily product. Complex **15** (410 mg, 0.73 mmol) and NEt_3 (2.5 mL, 17.9 mmol) were then suspended in degassed *m*-xylene (25 mL), flushed with argon, followed by the addition of Cl_3SiH (2.2 mL, 21.8 mmol) via a syringe. The reaction vessel was then closed and stirred at 120 °C for 14 h. After it was cooled to room temperature, the reaction mixture was poured into a degassed 2 N NaOH (100 mL) solution, extracted with dry toluene (2 × 100 mL), and dried over anhydrous Na_2SO_4. Solvent removal afforded a light yellow oily product, which was redissolved in a mixture of CH_2Cl_2 (5 mL) and CH_3CN (10 mL). $PdCl_2(NCPh)_2$ (220 mg, 0.57 mmol) was added, and the resulting mixture was stirred at room temperature for 30 min, followed by the addition of $AgBF_4$ (485 mg, 2.49 mmol) in one portion. After it was stirred for an additional 30 min, the mixture was diluted with CH_2Cl_2 (250 mL) and stirred with a saturated brine solution (200 mL) for 5 h. The organic layer was separated, dried over Na_2SO_4, and passed through a short silica gel column. Solvent removal and recrystallization from CH_2Cl_2/Et_2O gave **16** as a yellow powder. Yield: 210 mg (55%). ^{1}H NMR (d_6-DMSO, 300 MHz): δ 8.01−7.87 (m, 4H), 7.71−7.40 (m, 16H), 7.08 (s, 2H), 5.88 (m, 1H), 5.21 (m, 2H), 4.10 (s, 2H), 3.75 (bs, 4H). Anal. Calcd for $C_{35}H_{31}ClOP_2Pd$: C, 62.61; H, 4.65; Found: C, 62.37; H, 4.52;

Synthesis of Palladium Chloride 1-[3-((3-(Trimethoxysilyl)propyl)sulfanyl)propoxy]-3,5-bis[(diphenylphosphanyl)methyl]benzene (17). Complex **16** (180 mg, 0.27 mmol), (3-mercaptopropyl)trimethoxysilane (53 mg, 0.27 mmol), and AIBN (10 mg) were mixed in dry $CHCl_3$ (25 mL), and the resulting mixture was refluxed under argon for 24 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure and the resulting yellow solid residue was washed with hexanes (2 × 10 mL) to afford **17** as a yellow crystalline solid. Yield: 200 mg (85%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.00−7.83 (m, 4H), 7.57−7.28 (m, 16H), 7.01 (s, 2H), 4.20 (m, 2H), 3.82 (bs, 4H), 3.54 (bs, 9H), 2.47 (m, 4H), 1.93 (m, 2H), 1.53 (m, 2H), 0.39 (m, 2H).

General Procedure for the Synthesis of Polymers 2 and 3. The respective monomers were dissolved in $CDCl_3$, followed by the addition of the desired amount of catalyst. The polymerization was monitored via NMR. After completion of the polymerization a few drops of ethyl vinyl ether were added. The polymer was then purified by reprecipitation from chloroform into cold methanol. The purification procedure was repeated until the resulting methanol solution became colorless. The methanol was then decanted and the resulting polymer dried in vacuo.

Polymer 2. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.8 (m, 10H), 7.34 (m, 12H), 6.49 (br s, 4H), 5.50−5.17 (br m, 2H), 4.23 (br s, 4H), 4.00−3.85 (m, 2H), 3.19−2.28 (br m, 3H), 2.01−1.55 (br m, 8H), 1.53−1.02 (m, 14H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 158.0, 149.8, 148.8, 133.9, 133.9, 131.9, 133.8, 132.4, 132.3, 132.2, 131.5, 131.4, 129.9, 129.7, 129.6, 128.1, 127.9,

Polymer 3. ^{1}H NMR (DMSO, 300 MHz): δ 7.7 (m, 10H), 7.4 (m, 12H), 6.6 (br s, 4H), 5.53−5.14 (br m, 2H), 4.5 (br m, 4H), 3.31 (s, 4H), 2.13 (br m, 2H), 1.45−0.88 (br m, 23H). ^{13}C NMR (DMSO, 300 MHz): δ 170.3, 158.0, 149.8, 148.8, 133.9, 133.9, 131.9, 133.8, 132.4, 132.3, 132.2, 131.5, 131.4, 129.9, 129.7, 129.6, 128.1, 127.9, 118.9, 113.7, 50.0, 36.4, 30.8, 29.7, 29.4, 25.2.

Synthesis of SBA-15 Palladium Chloride 1-[3-((3-(Trimethoxysilyl)propyl)sulfanyl)propoxy]-3,5-bis[(diphenylphosphanyl)methyl]benzene (4). Complex **17** (200 mg, 0.23 mmol) was mixed with SBA-15 (1.0 g) in dry toluene (50 mL), and the mixture was stirred at room temperature for 24 h, at which point the mixture was filtered and washed extensively with DMF and CH_2Cl_2 and then dried under high vacuum to afford **4**. Elemental analysis indicated a palladium loading of 0.12 mmol of Pd/g of support. FT-Raman (spectrum in the Supporting Information): 3061 (aromatic C−H), 2936 (aliphatic C−H), 1024 (C−O stretching, CH_2OAr), 664 (C−S stretching, CH_2SCH_2) cm^{-1}.

General Procedure for the Catalysis. The reaction was carried under an inert atmosphere using freshly distilled NEt_3 and DMF. A vial was loaded with the catalyst, *n*-butyl acrylate, iodobenzene, and DMF. The solution was heated to 120 °C. When the temperature reached 120 °C, triethylamine was added in one portion to the solution, at which point time 0 was taken for the kinetic data analysis.

Mass Spectroscopy. In a reaction flask, catalyst **1** (23.5 mg, 0.035 mmol) and dicyclohexylmethylamine (13.6 mg, 0.07 mmol) were dissolved in DMF. The reaction mixture was heated to 120 °C and stirred for 1 h before an aliquot (0.007 mL) was removed from the vessel and analyzed via ESI mass spectroscopy (MS-ESI). Another 2 equiv (based on **1**) of dicyclohexylmethylamine was added to the reaction mixture, which was stirred for an additional 1 h before another aliquot was taken and analyzed by MS-ESI. The same operation was repeated for 24 h. ESI mass spectroscopy spectra of all aliquots showed molecular ion signals at *m/z* 182.3.

Acknowledgment. We thank the U.S. Department of Energy, Basic Energy Sciences, for financial support through Catalysis Science Grant/Contract No. DE-FG02-03ER15459. The X-ray absorption spectroscopy research was carried out in part at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences, under Contract Nos. DE-AC02-98CH10886 and DE-FG-03ER15460.

Supporting Information Available: Text, figures, and tables giving a detailed description of the XAS results and the *XYZ* coordinates of all computational experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

OM048992V