Evidence that SCS Pincer Pd(II) Complexes are only Precatalysts in Heck Catalysis and the Implications for Catalyst Recovery and Reuse

Kunquan Yu,[a] William Sommer,[b] John M. Richardson,[a] Marcus Weck,[b,*] Christopher W. Jones[a, b,*]

[a] School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA
Fax: (+1)-404-894-2866, e-mail: cjones@chbe.gatech.edu
[b] School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, USA
E-mail: marcus.weck@chemistry.gatech.edu

Received: August 20, 2004; Accepted: September 29, 2004; Published online: January 11, 2005

Abstract: SCS-pincer Pd(II) complexes have been covalently immobilized onto porous silica, cross-linked polymer (Merrifield resin) and soluble poly(norbornene) supports *via* either amide or urea linkages and evaluated in the Heck coupling of iodobenzene with *n*-butyl acrylate. Kinetic experiments and poisoning studies indicate that in all cases the pincer complexes merely act as precatalysts. Contrary to literature reports, there is no evidence for catalysis by the intact amide-linked SCS-Pd(II) complexes under any conditions studied here.

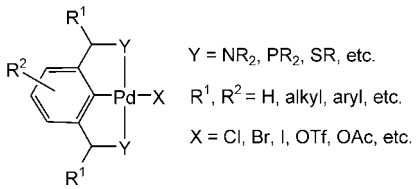
Keywords: biphasic catalysis; Heck reaction; immobilization; leaching; palladium; pincer complex

Introduction

Heck coupling is an important carbon-carbon bond forming reaction that is most often catalyzed by palladium catalysts. Both homogeneous and heterogeneous[1] precatalysts have been employed. Traditional heterogeneous catalysts, such as Pd(II)-exchanged oxides or resins[2] or Pd(0) on standard supports such as activated carbon[3] or oxides[4] have been used. In addition, metallic Pd nanoparticles[5] have also been employed as homogeneous or quasi-homogeneous systems. Despite the preponderance of solid catalysts for Heck reactions, the development of stable, recyclable supported catalysts remains an important goal. This is due to the fact that, for many heterogeneous "catalysts", there is substantial evidence that leached/dissolved Pd species are the true active species.[3,6] However, in other studies it is maintained that all the evidence supports heterogeneous active species.[4a,7] If a truly heterogeneous catalyst that can be conclusively shown to impart no leached metal species into solution were developed, this would be a major advance, as residual metal contamination is the primary drawback of current Heck catalysis techniques.

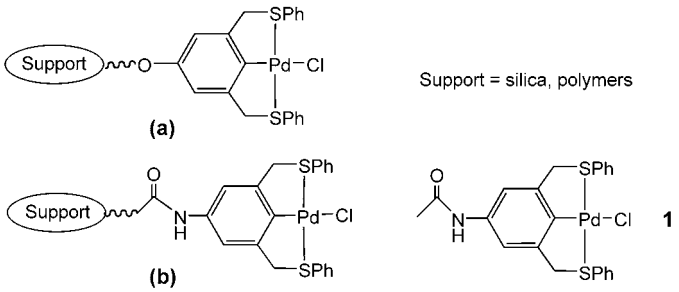
One of the most promising, well-defined transition metal catalysts for Heck and Suzuki coupling reactions are Pd(II) pincer complexes (SCS, NCN, PCP) (Scheme 1).[8] It has been suggested that these catalysts are quite stable compared to other precatalysts because they are stable in organic solvents at elevated temperatures and they can effectively promote Heck reactions in air. Indeed, in recent years several elegant examples of Heck catalysis by "recyclable catalysts" based on polymer immobilized SCS pincer Pd complexes have been reported,[9] where the "catalysts" are shown to be capable of promoting the Heck coupling reaction of iodoarenes and terminal olefins even in the presence of air. Furthermore, the supported species was used repeatedly with little or no decrease in reaction yields.[9] However, some SCS pincer Pd(II) complexes, such as those with an ether linkage between the complex and the support (Scheme 2, **a**), have been shown to decompose under reaction conditions.[9a,10]

Despite the observations of complex decomposition with SCS pincer Pd(II) complexes with ether linkages (SCS-O), similar complexes with subtly different ligand structures including an amide-containing linkage (Scheme 2, **b**) to the support are reported to promote Heck reactions in multiple uses, implying that they are recyclable catalysts.[9] Indeed, results similar to those re-



Scheme 1. Pincer palladium(II) complexes.

 DOI: 10.1002/adsc.200404264



Scheme 2. SCS-N pincer Pd(II) complexes.

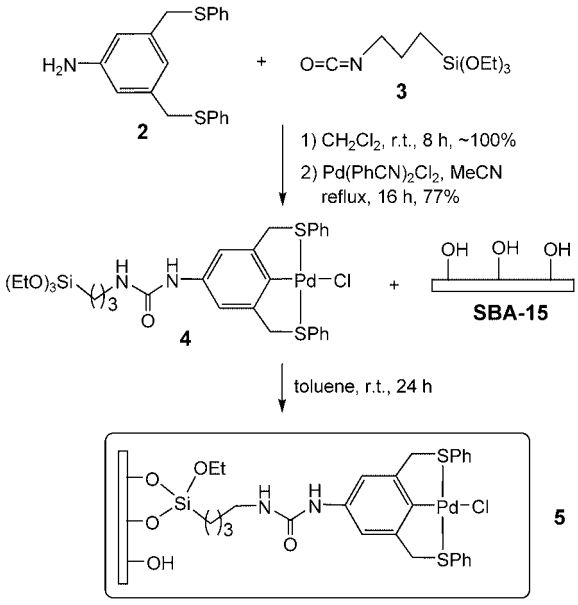
ported in the literature have been replicated on polymer and silica supported amide-linked SCS pincer Pd(II) complexes in our laboratories. As in previous reports, solids containing tethered Pd(II) SCS-N pincer complexes can be added to reaction media to promote the Heck reaction of iodoarenes and acrylates and following the reaction, the solids can be recovered and subsequently used to promote additional Heck reactions giving similar yields. However, further experimentation presented here indicates that the notion that these immobilized complexes are acting as recyclable catalysts is false.

By combining the study of homogeneous, soluble poly(norbornene), insoluble Merrifield resin and insoluble porous silica materials as supports for SCS pincer Pd(II) complexes, we have obtained compelling evidence that immobilized Pd-SCS pincer complexes merely serve as *recoverable and reusable Pd(II) precatalyst sources* that effectively leach Pd species into solution. The resulting soluble Pd(0) species, as in the related half-pincer complexes previously described,[11] are the true catalytic species and we find no evidence for catalytic activity by intact SCS pincer Pd complexes. These results also rule out a possible Pd(II)-Pd(IV) catalytic cycle[8f, 12] that has been proposed as the catalytic cycle for SCS Pd(II) Heck reactions with these "catalysts". This behavior was not likely apparent in previous studies due to the more limited scope of the catalysts employed. Especially with soluble polymeric precatalysts,[9] this observation would be difficult to discern because critical tests such as filtration tests could not be performed reliably.

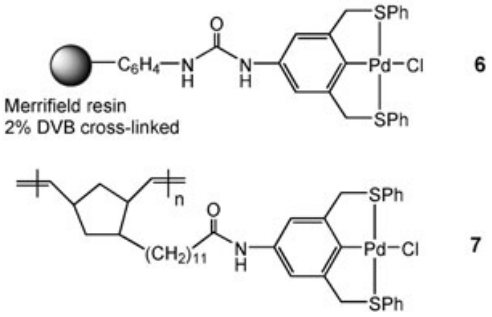
Results and Discussion

Synthesis

As noted above, simply changing the support linkage from an ether group to an amide one (Scheme 2, **b** and **1**) has been suggested to drastically alter the behavior of SCS-Pd complexes and yield stable and recyclable catalysts.[9a] To this end, complex **1**[9a] and its supported derivatives were synthesized and evaluated in the Heck reaction as described below.



Scheme 3. Synthesis of precatalyst **5**.



Scheme 4. Supported SCS-N pincer complexes.

Porous silica, soluble poly(norbornene) and insoluble Merrifield resin-supported SCS-N pincer Pd(II) complexes with either an amide or urea linkage were prepared, as shown in Schemes 3 and 4. Reaction between the SCS-NH_2 complex **2** with 3-isocyanopropyltriethoxysilane **3** yields an SCS pincer complex with an $Si(OEt)_3$ end group in quantitative yield; palladation was carried out in refluxing acetonitrile to afford complex **4** with a urea linkage at the 4 position in its aromatic ring. The homogeneous SCS pincer Pd(II) complex **4** was covalently immobilized onto mesoporous silica support, e.g., SBA-15, utilizing a reaction between the -$Si(OEt)_3$ group with surface silanols to form Si–O–Si bonds with the concomitant release of ethanol (Scheme 3). A typical loading for the SBA-15 supported complex **5** is approximately 0.10 mmol Pd per gram support. Extensive washing with DMF and CH_2Cl_2 and filtration tests[13] indicated that essentially all the SCS pincer Pd(II) in **5** is covalently bonded to the silica surface.

Similarly, contacting **2** with isocyanate modified Merrifield resin, followed by metallation with $Pd(PhCN)_2Cl_2$

in refluxing MeCN afforded an insoluble Merrifield resin supported pincer Pd complex **6** (Scheme 4). The poly(norbornene)-immobilized **7** (Scheme 4) was synthesized in 5 steps starting from **2** and cyclobutadiene. Complex **7** is a close replicate to the PEG supported materials previously reported,[9a] as both polymer supports have an amide linkage (in contrast to the urea linkage in **5** and **6**) and are soluble under reaction conditions.

Heck Catalysis

All Heck coupling reactions were carried out using *n*-butyl acrylate (2.74 mmol) and iodobenzene (1.37 mmol) in DMF (5 mL) at 120 °C using NEt_3 (2.06 mmol) as base.

Distinguishing Between Homogeneous and Heterogeneous Catalysis

There is a substantial body of work dedicated toward distinguishing between homogeneous and heterogeneous catalysis. For example, Finke has recently reviewed the methodologies for distinguishing between catalysis by metal nanoparticles and metal complexes when starting with metal complexes of easily reducible metals (Pd, Pt, Ru, etc.) in hydrogenation reactions.[14] By utilizing a combination of experimental tests including kinetic investigations, filtration tests, and poisoning studies, in many cases it is possible to conclusively determine the nature of the true active species. A number of the techniques outlined in the excellent review by Finke are used here to show that the intact Pd(II) SCS-N pincer complex is not the active species in Heck catalysis.

Complex **1** was found to be highly active in the Heck coupling of *n*-butyl acrylate and iodobenzene, giving quantitative conversion of the limiting reactant iodobenzene in merely 10 min. However, in the presence of excess Hg(0) (molar ratio to [Pd] ~ 300), **1** was completely inactive, as shown in Figure 1D. If the Heck reaction were promoted by the intact Pd(II) SCS-N pincer complex, a hypothetical Pd(II)-Pd(IV) cycle would be expected and Hg(0) should not affect the reaction, as it is used as a poison for Pd(0) species. The ability of Hg(0) to poison metal particle heterogeneous catalysts, by amalgamating the metal or adsorbing on the metal surface, has been known for many years.[14,15] However, Hg(0) is not expected to have a poisoning effect on molecular homogeneous organometallic complexes containing metals in high oxidation states that are tightly bound by protective ligands, especially pincer complexes that utilize a hypothetical Pd(II)-Pd(IV) cycle.[12] Although this assumption about Hg(0) is widely held, it is rarely probed. To probe this, a chemical transformation where the complex is known to remain bound to organic ligands in an elevated oxidation state must be carried out in the presence of Hg(0). In the case of Pd SCS pincers, Weck and Pollino[16] have shown that poly(norbornene) supported cationic pincer SCS Pd(II) species can serve as a recognition unit for self-assembly with pyridines. We find that this coordination is not disrupted in the presence of excess Hg(0). For example, after Cl abstraction of **8** with $AgBF_4$, coordination still occurs between the resulting cationic Pd(II) pincer complex and pyridine molecule (Scheme 5), as determined by ^1H NMR. This gives clear evidence that Hg(0) is not interacting with the Pd(II) metal center in the pincer complex and this is unlikely the mechanism for catalyst poisoning in the presence of Hg(0).

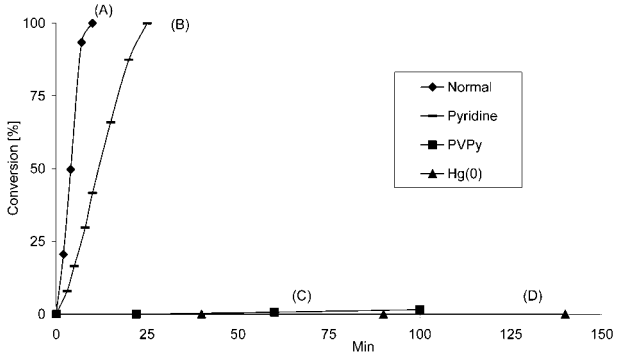
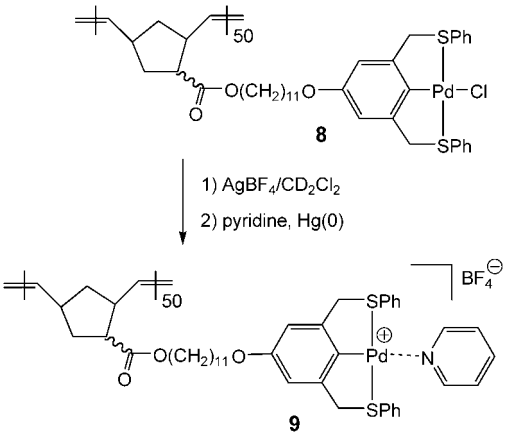


Figure 1. Conversion of iodobenzene as a function of time for the Heck catalysis with **1** under normal conditions (A), in the presence of 150 equivs. pyridine (B), in the presence of 300 equivs. PVPy (C), and in the presence of excess Hg(0) (~300 equivs.) (D). All reagents ratios are relative to complex **1**.



Scheme 5. Coordination between poly(norbornene)-SCS-PdCl (**8**) and pyridine. Self-assembly experiment was carried out by adding 1 equiv. of $AgBF_4$ to a CD_2Cl_2 solution of **8** and the solution was filtered 3 times through celite to remove the AgCl precipitate. The cationic Pd(II) pincer complex was then added into a stirred mixture of Hg(0) (20 equivs.) and pyridine (1 equiv.) in CD_2Cl_2. The solution turned light green. Solvent removal and drying under vacuum yielded a light green complex. Coordination was confirmed by ^1H NMR.[16]

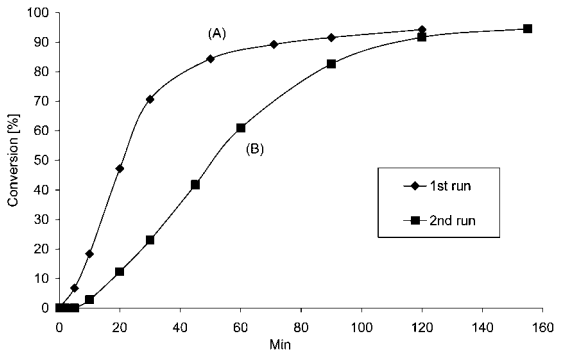


Figure 2. Conversion of iodobenzene as a function of time for the first (A) and second (B) Heck reaction runs with **5**.

The lack of activity of complex **1** in the presence of Hg(0) provides the first evidence that **1** likely decomposes under reaction conditions to form soluble Pd(0) species and that Hg(0) interactions with these Pd moieties completely terminate the reaction. In addition, a color change from light yellow to reddish-orange was observed during the Heck reaction with **1** and the intensity of the reddish-orange color correlates with the increased conversion of the reactants. As soluble colloidal palladium nanoparticles often impart a reddish-orange tint in DMF,[11f] this further suggests a breakdown of the pincer-Pd bonds to liberate metallic Pd species. This hypothesized decomposition motivated further study of supported analogues.

The immobilized complex **5** exhibited high activity for the Heck reaction, and a 93% GC conversion of iodobenzene was achieved in 2 h. After recovery, a similar yield of 92% conversion was also obtained in 2 h when the recovered **5** was reused in a subsequent Heck reaction. However, a closer look at the kinetic plots (Figure 2) revealed that the recovered complex **5** has a much longer induction period and much lower early stage activity in comparison to the first run. Indeed, the sigmoidal kinetic plot shown in Figure 2 is consistent with catalysis by Pd nanoparticles whereby the active nanoparticles are generated by an autocatalytic growth process.[14,17] Elemental analysis of the solid before and after the 1st use indicated that 6.7% of the immobilized palladium was lost. Since all the palladium is covalently bonded to the support before reaction,[13] one must conclude that some of the supported Pd metal is leached out into the solution during the reaction.

Thus, if proof of recyclability is based solely on reaction yields, one might suggest that **5** is a recyclable catalyst. However, the kinetic data clearly indicate that decomposition took place. A filtration test confirms the presence of soluble leached active palladium species. In this control experiment, a Heck reaction performed with **5** was interrupted, and the solid was filtered while hot under argon after achieving 38% conversion of iodobenzene. Subsequently, fresh reagents were added to the filtrate and it was observed that the Heck reaction continued at about half the reaction rate prior to the solid removal. In addition to this filtrate activity, the recovered solid is also shown to retain activity for the Heck reaction, as has been reported in previous works.[9a,f]

The above data clearly show that some complex decomposition takes place and that an active, soluble Pd(0) species is likely formed. However, the data described above do not rule out the possibility of a fraction of the catalysis occurring at intact Pd(II) SCS-N pincer sites that are still attached to the solid support. To probe this, a poison that effectively quenches only homogeneous catalysis is needed. Insoluble cross-linked poly(vinylpyridine) (PVPy) has been shown to be an excellent scavenger for soluble molecular Pd[10,18] [and potentially also for soluble Pd(0) nanoparticles[10]], most likely due to its excellent ligand binding ability to Pd and insolubility under reaction conditions. The addition of insoluble PVPy to the reaction mixture containing **5** should preferentially shut down catalysis due to homogeneous Pd, without affecting sites that are covalently bound to the SBA-15 support if the assumption that PVPy cannot access the pores of SBA-15 is correct. To probe this assumption, PVPy was used as a basic poison in the acid-catalyzed dimerization of α-methylstyrene.[19] As shown in Table 1, when a silica-tethered sulfonic acid catalyst is used (with an average pore size larger than the SBA-15 used here), the addition of PVPy (150 equivs., molar ratio to acid sites) results in only a slight decrease of its activity, likely due to some poisoning of acid sites on the external surface. In contrast, molecular pyridine (150 equivs.) almost completely quenches its activity. This gives evidence that PVPy cannot access the acid sites in the mesopores of the support and provides some foundation to the notion that it may be used as an effective poison for exclusively soluble, accessible species.[20]

It was found that in the presence of excess PVPy (150 equivs.), less than 1% iodobenzene conversion was observed for **5** even after 2.5 h. This suggests that the catalytic activity from **5** stems solely from leached/unsupported Pd species that are soluble in DMF. Furthermore, in the presence of excess of Hg(0), no Heck activity was observed with **5**. This provides additional evidence that **5** likely decomposes under reaction conditions to form soluble Pd(0) species.

Thus, no Heck activity is observed from the intact pincer-Pd **5** under any conditions used here. As the pincer Pd complex in **5** is immobilized on a silanol-containing oxide surface and these groups could interact with the Pd complex, potentially aiding complex decomposition, the examination of other, more inert supports is also important. Therefore, the Heck activity of the insoluble Merrifield resin supported **6**, where pincer Pd complexes are attached to a cross-linked polymeric network, was also evaluated.[21] Material **6** is also highly active for the Heck reaction of *n*-butyl acrylate and iodobenzene, a 92% GC conversion of iodobenzene was achieved in

Table 1. Summary of tests and observations.

Case	Catalyst	Test	Observations and Implications
i	**1**	Hg(0) – Heck	No reactivity. Catalysis occurs *via* a classic Pd(0)-Pd(II) cycle or Hg(0) reacts with the Pd(II) precatalyst.
ii	**1**	PVPy – Heck	No reactivity. PVPy blocks access to Pd sites or removes Pd species from solution.
iii	**1**	Pyridine – Heck	High activity. PVPy must poison by removing Pd sites from solution.
iv	**8**	Hg(0) – pyridine self-assembly	Hg(0) does not inhibit the coupling, implying Hg(0) has no affect on Pd(II) intermediates.
v	**5**	Hg(0) – Heck	No reactivity. Catalysis occurs *via* a classic Pd(0)-Pd(II) cycle.
vi	**5**	PVPy – Heck	No reactivity. PVPy blocks access to Pd sites. All sites are homogeneous, no evidence for catalysis by intact Pd(II) SCS-N pincers.
vii	**5**	Filtration test – Heck	Filtrate shows high activity, giving evidence for catalysis by leached, soluble species.
viii	**5**	Recycle of **5** – Heck	Slightly reduced activity. Solid is a reusable precatalyst or catalyst. Kinetics are indicative of potential formation of a Pd(0) nanoparticle catalyst.
ix	**6**	Hg(0) – Heck	No reactivity. Catalysis occurs *via* a classic Pd(0)-Pd(II) cycle.
x	**6**	PVPy – Heck	No reactivity. PVPy blocks access to Pd sites.
xi	**7**	Hg(0) – Heck	No reactivity. Catalysis occurs *via* a classic Pd(0)-Pd(II) cycle.
xii	**7**	PVPy – Heck	Very little reactivity. PVPy blocks access to Pd sites.
xiii	Silica-propyl-SO_3H	AMS coupling	High activity. 97% conversion of AMS in 2 h.
xiv	Silica-propyl-SO_3H	PVPy – AMS coupling	High activity, 83% conversion of AMS in 2 h. PVPy cannot enter the pores of the support.
xv	Silica-propyl-SO_3H	Pyridine – AMS coupling	Low activity, 4% conversion of AMS in 2 h. Pyridine can enter the pores of the support and neutralize the acid sites.

only 25 min. Similar poisoning studies on **6** showed that in the presence of PVPy (150 molar equivs.), less than 1% iodobenzene conversion was achieved after 3 h, and with excess Hg(0), no Heck product was detected even after prolonged reaction times. This gives evidence that **6** behaves like its silica supported analogue **5**, and that all the Heck activity stems from the leached/unsupported Pd(0) species.

Soluble poly(norbornene)-immobilized **7** also exhibited high activity for the Heck coupling of iodobenzene and *n*-butyl acrylate, as 99% GC conversion of iodobenzene was achieved within 60 min. However, in the presence of excess Hg(0) (~500 equivs.) no Heck activity was observed and with PVPy (150 equivs.), only 6% GC conversion of iodobenzene was achieved with a reaction time of 3 h in both cases. This suggests that **7** acts like its silica and Merrifield resin supported insoluble analogues **5** and **6**. Contrary to literature reports that SCS pincer Pd(II) complexes with an amide linkage are stable and recyclable, the soluble polymer-supported catalyst used here (**7)** merely acts as a precatalyst. Indeed, more recent reports of Heck catalysis by polymer-bound SCS Pd pincer complexes[22] indicate that catalysis by homogeneous Pd colloids cannot be excluded.

The fact that PVPy shuts down the Heck activity of both insoluble **5** and **6** suggests that likely a similar mechanism was also adopted on the homogeneous complex **1** (Figure 1C), even though it is less straightforward in light of the soluble nature of **1**. In the presence of 300 equivs. PVPy (molar ratio of pyridine unit to [Pd]), less than 1% iodobenzene conversion was achieved even after 100 min (Figure 1C). As complex **1** was soluble under reaction conditions, the pyridine unit in PVPy could potentially block the coordination site of the Pd active species, inhibiting any catalytic reaction. If this assumption is true, addition of molecular pyridine during the reaction should suppress the catalytic activity of **1** even more, since the interaction between **1** with soluble pyridine would be much easier than that with the insoluble PVPy. To test these possibilities, a Heck reaction was performed with **1** in the presence of 150 equivs. pyridine and 100% conversion of iodobenzene was observed with only a slightly slower rate than a Heck reaction under normal conditions (Figure 1A and B). This rules out the possibility that the mechanism by which PVPy is poisoning the reactivity is by interacting with intact SCS pincer Pd(II) sites. More likely, soluble Pd species are leached from the SCS complex and these species are removed from solution by the insoluble PVPy and the activity difference (Figure 1B and C) observed is due to the solubility difference of the as formed Pd-pyridine and Pd-PVPy complexes under the reaction conditions used here.

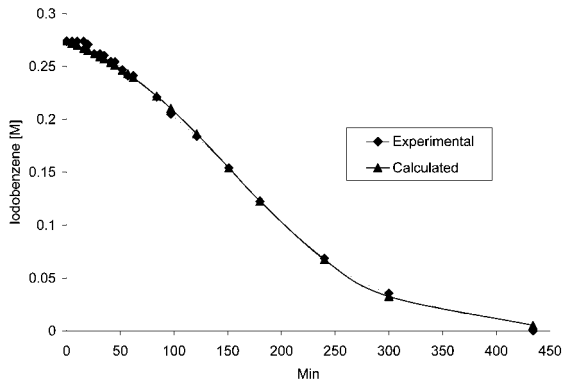


Figure 3. Iodobenzene loss *vs.* time curve and curve fit demonstrating the reasonable fit of the data to the nanoparticle-catalyzed reaction. The experimental data were collected with complex **1** (4.03×10^{-6} mol) at 85 °C using 1.37 mmol iodobenzene, 2.74 mmol *n*-butyl acrylate, NEt_3 (2.06 mmol) and *n*-dodecane (0.1 mL) in DMF (5 mL).

As noted above, the kinetics of the reaction are sigmoidal and this is consistent with catalysis by Pd nanoparticles.[14,17] Although it is not our intent to conclusively prove that molecular Pd(0) "naked" species[3b–d,23] or Pd(0) nanoparticles[5a,24] are the true active species (rather, we simply aim to show that intact Pd(II) SCS-N pincer species are not active), a brief discussion of the kinetics of the reaction is warranted.

Following the work of Finke[14,17] and others,[25] for catalysis by *in situ* formed metal nanoparticles, the rate is expected to be limited by the formation of the catalytic nanoparticles. In this case, the rate of product formation will follow the kinetic model for metal-particle formation. Typically, nanoparticle formation can be modeled using the combination of a nucleation pseudo-elementary step, A → B (rate constant k_1) followed by an autocatalytic surface-growth pseudo-elementary step, A + B → 2B (rate constant k_2), whereby metal species are added to a soluble nanoparticle [where A is the pincer complex and B is soluble Pd(0)]. When combined with the pseudo-elementary step for the Heck reaction, B + olefin + iodoarene → B + HI + coupling product, these steps can be fit to the kinetic data. Figure 3 depicts the concentration of iodobenzene as a function of time using complex **1**. In addition, the least-squares fit of the data using the above pseudoelementary kinetic model[17] is also plotted in Figure 3. It is evident that a close match is possible, giving pseudo-elementary rate constants of $k_1 = 0.014\ \text{min}^{-1}$ and $k_2 = 216\ \text{M}^{-1}\ \text{min}^{-1}$. It is noteworthy that the induction period that is commonly observed in these Heck reactions could be due to the slow formation of catalytic Pd(0) nanoparticles. This kinetic fit, along with the observation that Pd solids form under reaction conditions with **1**, is strong evidence that Pd nanoclusters may be the true catalytic species.

However, these observations cannot be taken as conclusive proof for catalysis by Pd nanoparticles, as other kinetic models can also lead to sigmoidal kinetics.[14] Indeed, a simple kinetic model for catalysis by molecular Pd(0) species: A → B, B + olefin + iodoarene → B + HI + coupling product [where A is the pincer Pd complex and B is soluble molecular Pd(0)] can also give a reasonable fit, with k_1 six orders of magnitude smaller than k_2. One might argue that there should be very little molecular Pd(0) species present in the reaction media, as the formation of nanoparticles from molecular Pd(0) species is thermodynamically downhill,[26] and thus most Pd in solution is likely in the form of nanoparticles.[27] However, formation of palladium black from soluble nanoparticles is also downhill yet in many cases nanoparticles are kinetically stable species that are metastable for long periods of time. Thus, given the tremendous turnover frequencies that are reported for some Heck reactions, it is possible that short-lived, metastable molecular Pd species in low concentration are the true active catalysts. Indeed, the observation that PVPy poisons the reaction may be more compatible with molecular active species that are easily ligated by the polymer than with nanoparticles. Additionally, the observation that turnover frequencies often increase as the amount of added palladium decreases also supports catalysis by molecular Pd.[23] Overall, there is compelling evidence both for catalysis with molecular Pd species as well as by soluble Pd nanoparticles. Nonetheless, based on all the data provided, it is clear that the Pd(II) SCS-N pincer complex is not the true catalytic species; rather it is a convenient precatalyst for catalytic Pd(0) species.[28]

Conclusions

In summary, we have provided compelling evidence using a number of soluble and insoluble supported SCS-N pincer palladium complexes that SCS-pincer complexes with amide linkages are not stable during Heck reactions and that tethered derivatives are not recyclable catalysts. In all cases studied, these SCS-N pincer Pd complexes simply act as precatalysts, decomposing into soluble palladium species that perform the catalytic reaction. Furthermore, these results suggest that the leached and soluble palladium species do not follow the suggested Pd(II)/Pd(IV) catalytic cycle.[12] These results in conjunction with our recently published results on SCS-O pincer complexes[10] indicate that all SCS pincer complexes are likely not stable during the Heck reaction and are therefore neither recyclable nor reusable Heck catalysts. Recyclable catalysts may nonetheless be derived from immobilized Pd(II) SCS-N pincer species if, and only if, the *in situ* produced Pd(0) species remain wholly with the support and do not freely leach into solution.

Experimental Section

General Procedures

All reactions with air- and moisture-sensitive compounds were carried out under dry nitrogen/argon atmosphere using an MBraun UniLab 2000 dry box and/or standard Schlenk line techniques. DMF, *n*-butyl acrylate and NEt_3 were distilled over calcium hydride. 5-Amino-isophthalic acid dimethyl ester (Aldrich Co.), poly(4-vinylpyridine) (2% cross-linked, Aldrich Co.), isocynate modified Merrifield resin (2% DVB, 200–400 mesh, ~2 mmol N/g) (Aldrich Co.) and 3-isocyanatopropyltriethoxysilane (Gelest, Inc.) were used as received. All other reagents 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 μm). The temperature program for GC analysis was the following: heating from 50 °C to 140 °C at 30 K/min and heating from 140 °C to 300 °C at 40 K/min under constant pressure with inlet and detector temperatures kept constant at 330 °C. ^{1}H and ^{13}C NMR (300 MHz) spectra were recorded on a Mercury VX instrument. FT-Raman spectra were obtained on a Bruker FRA-106. At least 128 scans were collected for each spectrum, with a resolution of 2–4 cm^{-1}. Elemental analyses (Galbraith Laboratories, Inc., TN) were used to determine the palladium loadings of silica and Merrifield resin supported precatalysts. SBA-15 (100 Å pore size) was synthesized following a literature method.[29] 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 dry box.

SCS-NH_2 Pincer Ligand (2)

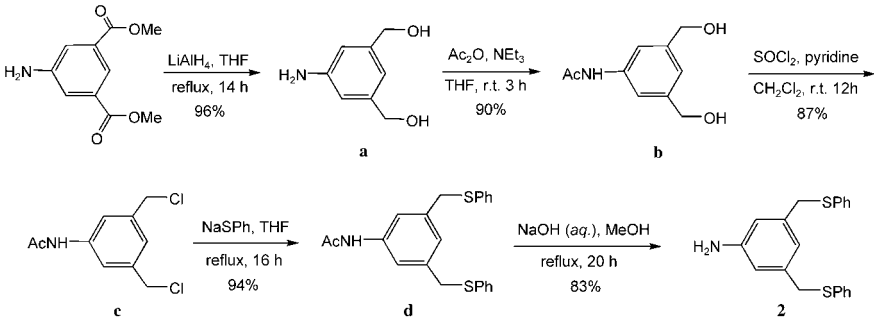
The ligand **2** was prepared in five steps as described in Scheme 6.

1. Synthesis of 3,5-bis(hydroxymethyl)aniline (a): A modified literature procedure was used for the synthesis of species **a**.[9a] 5-Amino-isophthalic acid dimethyl ester (2.0 g, 9.57 mmol) in 20 mL dry THF was slowly added into a THF (100 mL) slurry of $LiAlH_4$ (2.2 g, 58.0 mmol) at 0 °C under vigorous stirring. After stirring at 0 °C for 30 min, the mixture was allowed to reflux for 14 h, at which point it was cooled to 0 °C. Ethyl acetate (total ~20 mL) was then slowly added into the grayish mixture under vigorous stirring to quench excess $LiAlH_4$ and *ca.* 15 mL H_2O were then added to hydrolyze the alumina salt. A color change from grayish to green then yellowish was observed. After stirring for another 1 h, the resulting slurry was filtered through a pad of silica gel using a coarse frit and washed with several portions of THF (3 × 100 mL). Solvent removal of the combined filtrate and washings afforded a yellow-brownish crude compound **a**. Further purification was achieved by recrystallization from THF/hexane; yield: 1.6 g (96%). ^{1}H NMR (THF-d_8): δ = 6.58 (1H, s, ArH), 6.53 (2H, s, ArH), 4.47 (4H, d, J = 5.7 Hz, OCH_2), 4.40 (2H, br, OH), 3.93 (2H, t, J = 5.85 Hz, NH_2).

2. Synthesis of* N*-acetyl-3,5-bis(hydroxymethyl)aniline (b) and* N*-acetyl-3,5-bis(chloromethyl)aniline (c): Species **b** and **c** were synthesized according to a previously reported procedure.[9a]

3. Synthesis of* N*-acetyl-3,5-bis(phenylthiomethyl)aniline (d): A modified literature procedure was used for the synthesis of compound **d**.[9a] Species **c** (500 mg, 2.14 mmol) was mixed with NaSPh (800 mg, 6.06 mmol) in 30 mL dry THF and refluxed for 16 h. At this point, the reaction mixture was cooled to room temperature and solvent was removed under reduced pressure. The residual material was extracted with CH_2Cl_2 (40 mL) and washed with saturated aqueous NaCl (2 × 15 mL) and NaOH (2 N, 1 × 15 mL) and dried over anhydrous $MgSO_4$. Solvent was removed under vacuum and it was then purified through a flash silica gel column to afford an orange-brown oily product **d**; yield: 760 mg (94%). ^{1}H NMR ($CDCl_3$): δ = 7.50 (2H, m, Ph), 7.36 (2H, s, ArH), 7.31–7.10 (8H, m, Ph), 6.99 (1H, s, ArH), 4.04 (4H, s, SCH_2), 2.14 (3H, s, CH_3).

4. Synthesis of 3,5-Bis(phenylthiomethyl)aniline (2): To a solution of compound **d** (760 mg, 2.01 mmol) in 15 mL methanol was added 1.2 mL 40% aqueous NaOH, and the resulting mixture was allowed to reflux for 20 h. After cooling to room temperature, solvent was removed under reduced pressure and 50 mL CH_2Cl_2 were added. The organic phase was washed with 3 × 10 mL H_2O and dried over anhydrous $MgSO_4$. Passing through a short silica gel column and recrystallization from THF/ hexanes afforded pure **2** as an orange yellow solid; yield: 560 mg (83%). ^{1}H NMR ($CDCl_3$): δ = 7.34–7.16 (10H, m, Ph), 6.64 (1H, s, ArH), 6.52 (2H, s, ArH), 3.99 (4H, s, SCH_2), 3.61 (2H, br, NH_2); ^{13}C NMR ($CDCl_3$): δ = 146.90, 138.91, 136.77,



Scheme 6. Synthesis of SCS-NH_2 (**2**).

129.68, 129.02, 126.39, 119.88, 114.55, 39.13 ppm; anal. calcd. for $C_{20}H_{19}NS_2$: C 71.17, H 5.67, N 4.15; found: C 71.09, H 5.63, N 4.12.

Silica-Immobilized Precatalyst (5)

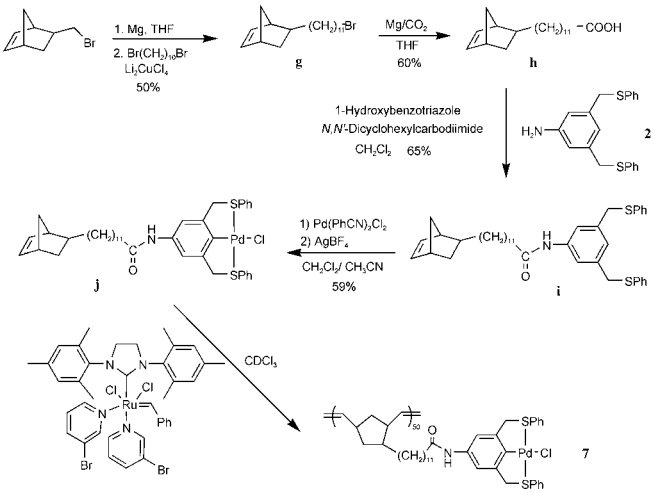
Compound **2** (200 mg, 0.593 mmol) was mixed with 3-isocyanatopropyltriethoxysilane (95%, 155 mg, 0.595 mmol) in 20 mL dry CH_2Cl_2. The mixture was allowed to stir at room temperature overnight and after solvent removal under reduced pressure, silane functionalized SCS ligand was obtained in a quantitative yield. ^{1}H NMR ($CDCl_3$): $\delta = 7.30-7.16$ (10H, m, Ph), 7.13 (2H, s, ArH), 6.95 (1H, s, ArH), 6.27 (1H, s, NH), 4.86 (1H, t, $J = 11.4$ Hz, NH), 4.01 (4H, s, SCH_2), 3.81 [6H, q, $J = 7.0$, $Si(OCH_2CH_3)$], 3.21 (2H, q, $J = 6.6$ Hz, CH_2), 1.62 (2H, m, $J = 7.6$ Hz, CH_2), 1.21 [9H, t, $J = 6.9$ Hz, $Si(OCH_2CH_3)$], 0.64 (2H, t, $J = 8.1$ Hz, $SiCH_2$); ^{13}C NMR ($CDCl_3$): $\delta = 155.41$, 139.10, 136.27, 129.93, 129.03, 126.56, 124.61, 119.91, 58.78, 43.06, 39.05, 23.83, 18.68, 8.01; anal. calcd. for $C_{30}H_{40}O_4N_2S_2Si$: C 61.61, H 6.89, N 4.79; found: C 61.34, H 7.12, N 4.72.

Silane-SCS (347 mg, 0.593 mmol) and $Pd(PhCN)_2Cl_2$ (227 mg, 0.593 mmol) were mixed in 20 mL dry acetonitrile and the resulting mixture was stirred at room temperature for 30 min and then refluxed for 16 h. The reaction mixture was filtered while hot to remove any insoluble materials. The solvent of the filtrate was removed under vacuum and the residuals were then washed with 2×10 mL hexanes to afford **4** as an orange yellow powder; yield: 330 mg (77%). ^{1}H NMR (DMSO-d_6): $\delta = 8.40$(1H, s, NH), 7.81 (2H, m, Ph), 7.46–7.15 (8H, m, Ph), 6.90 (2H, s, ArH), 6.10 (1H, s, NH), 4.79 (4H, s, SCH_2), 3.72 [6H, m, $Si(OCH_2CH_3)$], 3.43 (2H, q, $J = 7.0$ Hz, CH_2), 1.48 (2H, m, CH_2), 1.16 [9H, t, $J = 6.9$ Hz, $Si(OCH_2CH_3)$], 0.51 (2H, t, $J = 8.1$ Hz, $-SiCH_2$); anal. calcd. for $C_{30}H_{39}O_4N_2S_2SiPdCl$: C 49.65, H 5.42, N 3.86; found: C 49.87, H 5.38, N 3.76.

Complex **4** (200 mg, 0.276 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 silica immobilized precatalyst **5**. Elemental analysis indicated a palladium loading of 0.10 mmol Pd per gram support. FT-Raman: $\delta = 3057$ (aromatic C–H), 2928 (aliphatic C–H) and 1582 (urea linkage) cm^{-1}.

Merrifield Resin-Immobilized Precatalyst (6)

Merrifield resin (2% DVB cross-linked, typical loading 2.0 mmol N/g, Aldrich Co.) (700 mg, ~1.4 mmol N) was mixed with **2** (100 mg, 0.296 mmol) in 20 mL CH_2Cl_2 and the mixture was stirred at room temperature for 24 h, at which point, it was filtered and washed with CH_2Cl_2 and then dried under high vacuum to afford the polymer-bound SCS ligand, which was then mixed with $Pd(PhCN)_2Cl_2$ (110 mg, 0.287 mmol) in 20 mL MeCN and refluxed for 16 h. After cooling to room temperature, the reaction mixture was filtered and washed extensively with DMF and CH_2Cl_2 to afford the polymer-bound precatalyst **6**. Elemental analysis indicated a palladium loading of 0.135 mmol Pd per gram support. FT-Raman: $\delta = 3054$ (aromatic C–H), 3003–2851 (aliphatic C–H), and 1583 (urea linkage) cm^{-1}.



Scheme 7. Synthesis of poly(norbornene)-immobilized complex **7**.

Poly(norbornene)-immobilized precatalyst (7)

The polymer **7** was prepared in five steps as described in Scheme 7.

5. Synthesis of 5-(11-bromoundecyl)bicyclo[2.2.1]hept-2-ene (g): To a stirred solution of THF (50 mL) and Mg (1.652 g, 67 mmol) was added norbornene methyl bromide (9.35 g, 50 mmol). The solution was refluxed for 10 h before being slowly added to a mixture of 1,10-dibromodecane (10 g, 100 mmol) and Li_2CuCl_4 (9 mL, 0.1 M in THF) in THF 100 mL) at $-10\,^{\circ}C$. The solution was allowed to stir for 24 h at room temperature, at which point it was then washed with ammonium chloride, extracted with diethyl ether ($3 \times$ 100 mL), dried over $MgSO_4$ and the solvent was removed under vacuum. The product was further purified by column chromatography (hexanes); yield: 7.48 g (50%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 6.08-6.05$ (m, 2H, CH=CH), 3.37 (t, $J = 6.9$ Hz, 2H, CH_2-Br), 2.72 (t, $J = 3.2$ Hz, 2H), 1.93 (m, 1H), 1.83 (m, 2H), 1.92 (m, 19H), 1.03 (m, 1H), 0.46 (m, 1H); ^{13}C NMR ($CDCl_3$, 300 MHz): $\delta = 136.6$, 135.9, 132.3, 49.5, 46.3, 45.4, 42.5, 41.8, 38.7, 36.6, 34.8, 33.9, 32.8, 32.4, 29.9, 29.6, 29.5, 28.8, 28.7, 28.2. HRMS (EI): $m/z = 327.1$; anal. calcd. for $C_{18}H_{31}Br$: C 66.04, H 9.54; found: C 66.33, H 9.59.

6. Synthesis of 12-bicyclo[2.2.1]hept-5-en-2-yl-dodecanoic acid (h): Magnesium (474 mg, 19.5 mmol) and THF (8 mL) were added to a flame-dried flask. Species **g** (5.8 g, 17.7 mmol) was then added in portions of 1 g each. A catalytic amount of 1,2-dibromoethane (1 mL) was added to activate the reaction. The reaction mixture was then refluxed for 12 h under argon. Then CO_2 gas was bubbled into the solution for 15 minutes and the color of the solution turned off-white. At this point, the solution was cooled to room temperature, the unreacted magnesium was removed and then solvent was removed under vacuum. The product was further purified using column chromatography (CH_2Cl_2) to yield **h** as an orange oil; yield: 3.1 g (60%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 9.05$ (br, 1H, OH), 6.06–5.88 (m, 2H, CH=CH), 2.71 (m, 2H), 2.30 (m, 2H), 1.93

(m, 1H), 1.59 (m, 1H), 1.79 (m, 1H), 1.59 (m, 2H), 1.22 (br, 19H), 0.47 (m, 1H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 179.7, 136.6, 135.9, 132.3, 49.5, 46.3, 45.4, 45.2, 42.5, 41.8, 38.7, 36.6, 34.8, 34.4, 33.1, 32.4, 29.9, 29.7, 29.5, 29.3, 29.1, 28.9, 28.7, 24.8; HRMS (ESI): *m/z* = 291.0.

7. Synthesis of 12-bicyclo[2.2.1]hept-5-en-2-yl-dodecanoic acid (3,5-bis-pheny lsulfanylmethylphenyl)-amide (i): Species **h** (242 mg, 0.83 mmol) and 1-hydroxybenzotriazole (112 mg, 0.83 mmol) were stirred in a mixture of methylene chloride (10 mL) and dimethyl formamide (0.5 mL) until complete dissolution of the benzotriazole was observed. *N,N′*-Dicyclohexylcarbodiimide (171 mg, 0.83 mmol) was then added to the solution followed by the addition of **2**. The reaction mixture was stirred for 9 h at room temperature. A precipitate was observed and filtered through a pad of celite. The solvent of the filtrate was removed and the product was further purified by column chromatography (v/v 1 : 10 ethyl acetate:hexane) to afford **i** as a yellow oil; yield: 330 mg (65%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.39 (s, 2H, ArH), 7.31–7.13 (m, 10 H, SPh), 6.97 (s, 1H, ArH), 6.11–5.89 (m, 2H, CH=CH), 4.01 (s, 4H), 2.7 (m, 2H), 2.32–2.27 (t, *J* = 7.4 Hz, 2H), 1.97–1.93 (m, 1H), 1.86–1.78 (m, 1H), 1.73–1.66 (m, 2H), 1.39–1.15 (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 = 171.2, 138.4, 138.1, 136.7, 136.6, 136.0, 132.2, 129.4, 128.7, 126.1, 124.7, 118.7, 49.5, 46.3, 45.4, 45.2, 42.5, 41.8, 38.7, 37.7, 36.6, 34.8, 33.1, 32.8, 32.4, 32.0, 29.9, 29.7, 29.5, 29.4, 29.3, 28.7, 25.6; HRMS (ESI): *m/z* = 612.3.

8. Synthesis of Pd-Cl, 12-bicyclo[2.2.1]hept-5-en-2-yl-dodecanoic acid (3,5-bis-phenylsulfanylmethylphenyl)-amide (j): $Pd(PhCN)_2Cl_2$ (92 mg, 0.24 mmol) was added to a stirred solution of **i** (150 mg, 0.24 mmol) in 15 mL CH_2Cl_2/CH_3CN (v/v: 1/2). The solution was stirred for 30 min before the addition of $AgBF_4$ (119 mg, 0.61 mmol) in one portion. After being stirred for another 30 min, the mixture was added to a brine solution (200 mL) and stirred for another 6 h. The organic layer was separated, dried over $MgSO_4$ and the solvent removed under vacuum to yield a yellow powder that was further purified by column chromatography (v/v = 9 : 1, CH_2Cl_2:methanol); yield: 138 mg (59%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.17 (s, 1H, ArH), 7.72 (d, *J* = 9.2 Hz, 4H, SPh, ArH), 7.29 (m, 8H), 6.08–5.88 (m, CH=CH, 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, 149.3, 136.6, 136.0, 132.2, 131.8, 130.9, 129.4, 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* = 782.9; anal. calcd. for $C_{40}H_{50}ClNO_2PdS_2$: C 61.37, H 6.44, N 1.79; found: C 61.06, H 6.48, N 1.84.

9. Polymerization procedure for the synthesis of 7: Monomer **j** (85 mg, 0.11 mmol) was dissolved in $CDCl_3$ and stirred before the addition of the ruthenium catalyst (2 mg, 0.002 mmol). The polymer precipitated out almost instantly. The reaction was stirred for another 20 min before the addition of ethyl vinyl ether (2 drops). The polymer was then washed with methanol to afford **7** as an orange solid; yield: 70 mg (82%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ = 9.63 (br, s, NH, 1H), 7.73 (br, s, 5H), 7.32 (br m, 8H), 5.4–5.1 (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, 149.4, 136.2, 131.9, 130.4, 129.3, 113.0, 50.0, 36.4, 30.8, 29.7, 29.4, 25.2.

Heck Reactions of *n*-Butyl Acrylate and Iodobenzene

All Heck coupling reactions were carried out using *n*-butyl acrylate (2.74 mmol) and iodobenzene (1.37 mmol) in DMF (5 mL) at 120 °C using NEt_3 (2.06 mmol) as base and dodecane (~0.15 g) as GC internal standard. Typically, pincer complexes **1**, **5–7** (molar ratio of [Pd] to iodobenzene ~ 1 : 350) were mixed with all the reagents except NEt_3 and preheated at 120 °C for *ca.* 15 min, at which point NEt_3 in 0.5 mL DMF was syringed into the reaction mixture. Conversion was followed through GC analysis by taking aliquots from the reaction mixture periodically (diluted with THF or acetone). Preheating under vigorous stirring was found to be critical to minimize induction periods as well as insure good saturation of the reaction media with PVPy and Hg(0) when it were used (*vide supra*). All reactions were carried out at 120 °C unless otherwise noted.

Acid-Catalyzed Dimerization of α-Methylstyrene (AMS)

Porous silica supported sulfonic acid was prepared according to a literature method.[30] 3-Mecaptopropyltrimethoxysilane (1.0 g) was added into a toluene suspension of silica (MS-3050, PQ Corporation, pore volume: 3.0 mL/g; BET surface area: 500 m^2/g; pore diameter 240 Å; and average particle size ~ 90 μ). The reaction mixture was stirred at room temperature for 24 h and was then filtered and washed with toluene and dichloromethane. TGA analysis on the dried solid gave a thiol loading at about 0.55 mmol/g and FT-Raman showed the presence of the −SH stretching at 2058 cm^{-1}. The immobilized mercaptopropyl groups were then oxidized by 30% H_2O_2 (in methanol/H_2O mixture) and followed by acidification by 0.1 H_2SO_4 to yield the immobilized sulfonic acid. FT-Raman showed the complete disappearance of the −SH stretching at 2058 cm^{-1}, indicating conversion of −SH to $-SO_3H$.

In a typical AMS dimerization experiment, 60 mg (~3.3×10^{-5} mol) of the silica supported sulfonic acid was added into a 0.50 g AMS and 4.5 g cumene mixture along with ~0.2 g dodecane (GC internal standard) and the reaction was carried out at 50 °C. Conversion of AMS was analyzed through GC chromatography.

Acknowledgements

The US DOE Office of Basic Energy Sciences is acknowledged for financial support through Catalysis Science Contract No. DE-FG02–03ER15459. This work was also partially supported under a National Science Foundation Graduate Research Fellowship, grant No. 0228234, to JMR. The authors thank Prof. Robert J. Davis at the University of Virginia for helpful discussions.

References and Notes

[1] Here we use the traditional definitions of homogeneous (soluble) and heterogeneous (insoluble) catalysts. The alternative definitions (homogeneous – single-site and heterogeneous – multi-site) introduced by a) J. Schwartz, *Acc. Chem. Res.* **1985**, *18*, 302; and refined by b) Y.

Lin, R. G. Finke, *Inorg. Chem.* **1994**, *33*, 4891; c) J. D. Aiken, Y. Lin, R. G. Finke, *J. Mol. Catal. A*. **1996**, *114*, 29 are not used.

[2] a) T. H. Bennur, A. Ramani, R. Bal, B. M. Chandra, S. Sivasankar, *Catal. Commun.* **2002**, *3*, 493; b) A. Molnar, A. Papp, K. Miklos, P. Forgo, *Chem. Commun.* **2003**, 2626; c) C. Mehnert, D. W. Weaver, J. Y. Ying, *J. Am. Chem. Soc.* **1998**, *120*, 12289; d) L. Djakovitch, K. Kohler, *J. Mol. Catal. A.* **1999**, *142*, 275; e) R. S. Varma, K. P. Naiker, P. J. Liesen, *Tetrahedron Lett.* **1999**, *40*, 2075; f) A. Corma, H. Garcia, A. Leyva, A. Primo, *Appl. Catal. A*. **2004**, *257*, 77; g) M. Dams, L. Drijkoningen, B. Pauwels, G. Van Tendeloo, D. E. De Vos, P. A. Jacobs, *J. Catal.* **2002**, *209*, 225; h) A. Nejjar, C. Pinel, L. Djakovitch, *Adv. Synth. Catal.* **2003**, *345*, 612. i) A. Biffis, M. Zecca, M. Basato, *Eur. J. Inorg. Chem*. **2001**, 1131.

[3] a) F. Zhao, B. M. Bhanage, M. Shirai, M. Arai, *Chem. Eur. J.* **2000**, *6*, 843; b) F. Zhao, B. M. Bhanage, M. Shirai, M. Arai, *J. Catal.* **2000**, *194*, 479; c) R. G. Heidenreich, J. G. E. Krauter, J. Pietsch, K. Kohler, *J. Mol. Catal. A*. **2002**, *182–183,* 499; d) K. Kohler, R. G. Heidenreich, J. G. E. Krauter, J. Pietsch, *Chem. Eur. J.* **2002**, *8*, 622; e) K. Kohler, M. Wagner, L. Djakovitch, *Catal. Today* **2001**, *66*, 105.

[4] a) B. M. Choudary, S. Madhi, N. S. Chowdari, M. L. Kantam, B. Sreedhar, *J. Am. Chem. Soc.* **2002**, *124*, 14127; b) R. L. Augustine, S. T. O'Leary, *J. Mol. Catal. A*. **1995**, *95*, 277.

[5] a) J. Le Bars, U. Specht, J. S. Bradley, D. G. Blackmond, *Langmuir* **1999**, *15*, 7621; b) R. Sablong, U. Schlotterback, D. Vogt, S. Mecking, *Adv. Synth. Catal.* **2003**, *345,* 333; c) E. H. Rahimm, F. S. Kamounah, J. Frederiksen, J. B. Christensen, *Nano. Lett.* **2001**, *1*, 499; d) L. K. Yeung, R. M. Crooks, *Nano. Lett.* **2001**, *1*, 14; e) K. P. Gopidas, J. K. Whitesell, M. A. Fox, *Nano. Lett.* **2003**, *3*, 1757.

[6] a) A. Biffis, M. Zecca, M. Basato, *Eur. J. Inorg. Chem.* **2001**, 1131; b) K. Kohler, M. Wagner, L. Djakovitch, *Catal. Today* **2001**, *66*, 105; c) F. Zhao, B. M. Bhanage, M. Shirai, M. Arai, *J. Catal.* **2000**, *194*, 479; d) A. Biffis, M. Zecca, M. Basato, *J. Mol. Catal. A: Chem.* **2001**, *173*, 249.

[7] a) A. Corma, H. Garcia, A. Leyva, A. Primo, *Appl. Catal. A* **2004**, *257*, 77; b) M. Dams, L. Drijkoningen, B. Pauwels, G. Van Tendeloo, D. E. De Vos, P. A. Jacobs, *J. Catal.* **2002**, *209*, 225.

[8] a) J. Errington, W. S. McDonald, B. L. Shaw, *J. Chem. Soc. Dalton Trans.* **1980**, 2312; b) M. Albrecht, G. van Koten, *Angew. Chem. Int. Ed.* **2001**, *40*, 3750; c) W. A. Herrmann, V. P. W. Bohm, C.-P. Reisinger, *J. Organomet. Chem.* **1999**, *576*, 23; d) A. S. Gruber, D. Zim, G. Ebeling, A. L. Monteiro, J. DuPont, *Org. Lett*. **2000**, *2*, 1287; e) D. Zim, A. S. Gruber, G. Ebeling, J. DuPont, A. L. Monteiro, *Org. Lett*. **2000**, *2*, 2881; f) D. Morales-Morales, C. Grause, K. Kasaoka, R. Redon, R. E. Cramer, C. M. Jensen, *Inorg. Chim. Acta* **2000**, *300–302*, 958; g) H. P. Dijkstra, N. Ronde, G. P. M. Van Klink, D. Vogt, G. Van Koten, *Adv. Synth. Catal.* **2003**, *345*, 364; h) E. Diez-Barra, J. Guerra, V. Hornillos, S. Merino, J. Tejeda, *Organometallics* **2003**, *22*, 4610; i) M. Matsugi, D. P. Curran, *Org. Lett*. **2004**, *6*, 2717; j) P. B. Silveira, V. R. Lando, J. Dupont, A. L. Monteiro, *Tetrahedron Lett*. **2002**, *43*, 2327; k) M. E. Van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759.

[9] a) D. E. Bergbreiter, P. L. Osburn, Y.-S. Liu, *J. Am. Chem. Soc.* **1999**, *121*, 9531; b) D. E. Bergbreiter, J. Li, *Chem. Commun.* **2004**, 42; c) D. E. Bergbreiter, P. L. Osburn, J. D. Frels, *J. Am. Chem. Soc.* **2001**, *123*, 11105; d) D. E. Bergbreiter, P. L. Osburn, A. Wilson, E. M. Sink, *J. Am. Chem. Soc.* **2000**, *122*, 9058; e) D. E. Bergbreiter, *Chem. Rev.* **2002**, *102*, 3345; silica-supported Pd-PCP pincer catalysts have also been reported: f) R. Chanthateyanonth, H. A. Alper, *J. Mol. Catal. A*. **2003**, 201, 23.

[10] K. Yu, W. Sommer, M. Weck, C. W. Jones, *J. Catal.* **2004**, *226,* 101.

[11] a) I. P. Beletskaya, A. N. Kashin, N. B. Karlstedt, A. V. Mitin, A. V. Cheprakov, G. M. Kazankoc, *J. Organomet. Chem.* **2001**, *622*, 89; b) W. A. Herrmann, K. Öfele, D. V. Preysing, S. K. Schneider, *J. Organomet. Chem.* **2003**, *687*, 229; c) M. Beller, T. H. Riermeier, *Eur. J. Inorg. Chem.* **1998**, 29; d) C. S. Consorti, M. L. Zainini, S. Leal, G. Ebeling, J. DuPont, *Org. Lett.* **2003**, *5*, 983; e) C. Rocaboy, J. A. Gladysz, *New J. Chem.* **2003**, *27*, 39; f) C. Rocaboy, J. A. Gladysz, *Org. Lett.* **2002**, *4*, 199 3; g) R. B. Bedford, C. S. J. Cazin, M. B. Hursthouse, M. E. Light, K. J. Pike, S. Wimperis, *J. Organomet. Chem.* **2001**, *633*, 173; also, for PCP pincer complexes: M. R. Eberhard, *Org. Lett*. **2004**, *6*, 2125.

[12] a) A. Sundermann, O. Uzan, J. M. L. Martin, *Chem. Eur. J.* **2001**, *7*, 1703; b) B. L. Shaw, S. D. Perera, E. A. Staley, *Chem. Commun.* **1998**, 1361; c) B. L. Shaw, *New J. Chem.* **1998**, *22*, 77; d) M. Ohff, A. Ohff, M. E. van der Boom, D. Milstein, *J. Am. Chem. Soc.* **1997**, *119*, 11687; the mechanism was previously ruled out for half-pincer complexes: e) V. P. W. Bohm, W. A. Herrmann, *Chem. Eur. J.* **2001**, *7*, 4191; f) J. A. Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller, R. H. Crabtree, *Organometallics* **2002**, *21*, 700; g) H. Nakai, S. Ogo, Y. Watanabe, *Organometallics* **2002**, *21*, 1674.

[13] As in previous works,[10] the precatalysts are extensively washed and extracted in hot solvents to insure that physisorbed species are removed from the materials before they are used in Heck reactions.

[14] J. A. Widegren, R. G. Finke, *J. Mol. Catal. A*. **2003**, *198*, 317.

[15] a) G. M. Whitesides, M. Hackett, R. L. Brainard, J. P. P. M. Lavalleye, A. F. Sowinski, A. N. Izumi, S. S. Moore, D. W. Brown, E. M. Staudt, *Organometallics* **1985**, *4*, 1819; b) C. Paal, W. Hartmann, *Chem. Ber*. **19 18**, *51*, 711.

[16] J. M. Pollino, M. Weck, *Org. Lett*. **2002**, *4*, 753.

[17] a) M. A. Watzky, R. G. Finke, *J. Am. Chem. Soc*. **1997**, *119*, 10382; b) K. S. Weddle, J. D. Aiken III, R. G. Finke, *J. Am. Chem. Soc*. **1998**, *120*, 5653; c) J. A. Widegren, J. D. Aiken III, S. Özkar, R. G. Finke, *Chem. Matter*. **2001**, 13, 312; d) J. A. Widegren, M. A. Bennett, R. G. Finke, *J. Am. Chem. Soc*. **2003**, *125*, 10301.

[18] S. Klingelhöfer, W. Heitz, A. Greiner, S. Osetreich, S. Förster, M. Antonietti, *J. Am. Chem. Soc*. **1997**, *119*, 10116.
[19] Q. Sun, W. E. Farneth, M. A. Harmer, *J. Catal.* **1996**, *164*, 62.
[20] We note that the temperatures and solvents used in the acid-catalyzed dimerization and in the Heck reaction are different. However, we have confirmed that PVPy is largely insoluble in DMF at reaction temperature using the following test. PVPy was heated in DMF at the reaction temperature for 30 min. The PVPy was subsequently removed by filtration and the remaining liquid was used as the solvent for a Heck reaction with added **1**. The kinetics of this reaction were unchanged compared to standard conditions using **1** as the precatalyst. Thus, there was no appreciable soluble PVPy in solution.
[21] With limited characterizations on material **6** (characterized by FT-Raman), we are not able to confirm that only the SCS-Pd pincer (with a Pd–C bond) was formed, and it is possible that small amount of coordination complex that does not have a Pd–C bond is formed during palladation.
[22] a) D. E. Bergbreiter, S. Furyk, *Green Chem.* **2004**, *6*, 280; b) J. D. Frels, *Ph. D. Dissertation* **2002**, Texas A&M University, College Station, TX.
[23] A. H. M. de Vries, J. M. C. A. Mulders, J. H. M. Mommers, H. J. W. Hendrickx, J. G. de Vries, *Org. Lett.* **2003**, *5*, 3285.
[24] a) S. P. M. T. Greci, R. C. Kwong, K. Mercado, G. K. S. Prakash, G. A. Olah, M. E. Thompson, *Chem. Mater.* **2000**, *12*, 1985; b) R. Narayanan, M. A. El-Sayed, *J. Am. Chem. Soc*. **2003**, *125*, 8340.
[25] C. A. Jaska, I. Manners, *J. Am. Chem. Soc*. **2004**, *126*, 9776.
[26] See footnote 10 in ref.[14]
[27] TEM images of the precursor complex **1** and the reaction solution were taken in an attempt to document potential nanoparticle formation (Pd black formation was documented visually in the reaction solution). However, the data proved to be inconclusive.
[28] These results, coupled with previous reports on Pd(II)-SCS-O complexes,[9a,10] imply that other Pd(II)-SCS complexes that are claimed to be recyclable and recoverable likely also decompose: D. P. Curran, K. Fischer, G. Moura-Letts, *Synlett* **2004**, 1379.
[29] D. Zhao, Q. Hou, J. Peng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc*. **1998**, *120*, 6024.
[30] W. D. Bossaert, D. E. De Vos, W. M. Van Rhijn, J. Bullen, P. J. Grobet, P. A. Jacobs, *J. Catal*. **1999**, *182,* 156.

