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Silica and polymer-tethered Pd–SCS-pincer complexes: evidence for precatalyst decomposition to form soluble catalytic species in Mizoroki–Heck chemistry

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

[a] School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA
[b] School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, USA

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Abstract

Palladium(II)–SCS-pincer complexes have been covalently immobilized on porous silica and polynorbornene supports and evaluated in the Mizoroki–Heck reaction of iodobenzene and *n*-butyl acrylate. Kinetic experiments and poisoning studies indicate that the pincer complexes decompose under reaction conditions via rupture of the palladium–ligand bonds to liberate active Pd(0) homogeneous species. There is no evidence for catalysis by the intact Pd(II) pincer complex under any conditions evaluated, ruling out a Pd(II)–Pd(IV) catalytic mechanism that has been postulated for palladacycle catalysts under the conditions used here.

Keywords: Heck; Leaching; Organometallic; Silica; Catalyst; Pincer; Palladium

1. Introduction

The Heck reaction is among the most important carbon–carbon bond forming reactions in use today, especially in the fine chemical and pharmaceutical industries. A number of different precatalysts have been utilized, with palladium being the metal of choice in most systems. Highly active, robust catalysts can be created from a number of different precatalysts and a catalytic mechanism involving Pd(0) and Pd(II) intermediates is well-established. Despite this, in many cases, the nature of the active species is not understood.

Both homogeneous and heterogeneous precatalysts have been employed and there is conflicting information in the literature concerning whether truly heterogeneous metallic Pd is capable of promoting the Heck reaction. Traditional heterogeneous catalysts have been employed, such as Pd(II)-exchanged oxides or resins [1–9] or Pd(0) on standard supports such as activated carbon [8,10–14] or oxides [4,7–12,14–16]. Polymer-immobilized Pd complexes [17–19] or metallic Pd nanoparticles [20–23] have also been employed as homogeneous or quasi-homogeneous systems. With many heterogeneous catalysts, there is substantial evidence that leached/dissolved Pd species (that could be colloidal [24] or molecular [25]) are the true active species [9–14] while in other studies it is maintained that all the data support insoluble active species [6,7,15]. One issue that complicates this analysis is that there is evidence that in some cases soluble palladium species are produced during the reaction and that after all reactants are consumed, these species redeposit back onto the support with varying efficiencies during Mizoroki–Heck and Suzuki–Miyaura reactions [13,26]. Thus, if standard tests for homogeneous catalysts such as (i) filtration tests and (ii) elemental analysis of the solution for Pd after reaction are the only methods used to discriminate between soluble and insoluble catalysts, it is possible that they could provide misleading evidence that rules out catalysis by soluble species [10–13,27]. Indeed, in a related system, when Ni/charcoal is used as a catalyst for Kumada couplings, there is evidence that homogeneous catalyst redeposition onto the support is rapid and easily missed [28]. If a truly heterogeneous catalyst that can be conclusively shown to impart no

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* Corresponding authors.
E-mail addresses: marcus.weck@chemistry.gatech.edu (M. Weck), cjones@chbe.gatech.edu (C.W. Jones).

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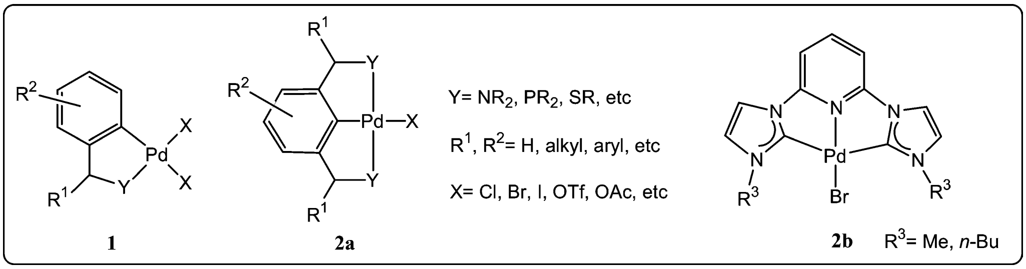

Scheme 1.

leached metal species into solution is developed, this would be a major advance, as residual metal contamination is the primary drawback of current Heck catalysis techniques.

A large variety of homogeneous precatalysts have been used in the Heck reaction. Simple Pd(II) phosphine complexes are common precatalysts that are in situ reduced to active Pd(0) species. Recently, the development of stable palladacycle complexes (Scheme 1) such as **1** (referred to here as a half pincer) or **2a** (referred to here as a pincer complex) or **2b** (referred to here as a CNC-pincer carbene complex) that are active in Heck catalysis has spurred a debate about a possible new mechanism in Heck catalysis [29–33]. Because these complexes are active for Heck catalysis and have very stable Pd–C bonds, it was surmised that perhaps they could potentially operate by a new Pd(II)–Pd(IV) catalytic process [31,34–37] instead of the generally accepted Pd(0)–Pd(II) cycle. New investigations of the half-pincer catalysts have shown that it is likely that these complexes are reduced to form soluble or insoluble Pd(0) catalytic species [33,38–43] and thus the Pd(II)–Pd(IV) cycle is unlikely [36,44]. However, for the pincer complexes, there is substantially less data available on the nature of the catalytic site and no clear picture of the catalytic cycle has emerged.[1]

A number of different Pd pincer complexes have been used as Heck precatalysts including SCS–Pd, NCN–Pd, PCP–Pd, and CNC–Pd complexes as shown in Scheme 1 [17–19,34,43,44,46–52]. The stability of these complexes in solvents tracks with the strength of the coordinating ligand, decreasing in the order CNC $>$ PCP $>$ NCN $>$ SCS, with the weakest of the pincer complexes still being substantially more stable than most other Pd(II) complexes with nonchelating ligands [53,54]. In an effort to establish recoverable, recyclable catalysts, Pd pincer complexes have been covalently immobilized on polymeric [17–19,46–49, 55] and silica [56] supports and ionically immobilized on clays [57]. In these cases, catalysis with immobilized catalysts was claimed and the catalysts were effectively recycled and reused [17,18,46–49,56,57]. Here we report a detailed study of covalently immobilized Pd–SCS-pincer complexes on polymeric and porous silica supports and show that for the systems studied here, there is no evidence for any heterogeneous catalysis[2] under the conditions reported.

2. Experimental

2.1. Materials and instrumentation

DMF was distilled from calcium hydride, and NEt$_3$ was distilled over molecular sieves. 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 and 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 to 140 °C at 30 K/min and heating from 140 to 300 °C at 40 K/min under constant pressure with inlet and detector temperatures kept constant at 330 °C. ^{1}H NMR (300 MHz) spectra were recorded on a Mercury VX instrument. A Netzsch Thermoanalyzer STA 409 was used for simultaneous thermal analysis combining thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) with a heating rate of 10 °C/min in air. 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}. X-ray photoelectron spectra (XPS) were collected using a Physical Electronics (PHI) Model 1600 XPS system equipped with a monochromator with an Al-K$_\alpha$ source ($h\nu = 1486.8$ eV). Ejected photoelectrons were detected by a hemispherical analyzer and the pressure in the spectrometer was below 5×10^{-9} Torr. For energy calibration, the carbon 1s binding energy was set to 285.0 eV. Transmission electron microscopy (TEM) images were obtained using a JEOL 100C operated at 100 kV.

SBA-15 (100 Å pore size) was synthesized following a literature method [61]. The as-prepared material was calcined using the following temperature program: (1) increasing the temperature at 1.2 °C/min to 200 °C, (2) heating at 200 °C for 1 h, (3) increasing at 1.2 °C/min to 500 °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

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[1] While this manuscript was under review, a manuscript was submitted that also addresses this issue with the related PCP-pincer system [45].

[2] Here we use the traditional definitions of homogeneous (soluble) and heterogeneous (insoluble) catalysts. The alternative definitions introduced by Schwartz [58] and refined by Finke and co-workers [59,60] are not used (homogeneous, single site; and heterogeneous, multisite).

box. The pore size and BET surface areas of SBA-15 were calculated from data gathered from N_2 physisorption experiments at 77 K using a Micromeritics ASAP 2010 system. TGA/DSC and elemental analyses were used to determine the organic loadings of precatalyst **5**.

2.2. Catalyst synthesis

*2.2.1. Palladation of 3,5-bis(phenylsulfanylmethyl) phenol (**3**)*

The SCS–OH pincer ligand was synthesized in five steps according to previously reported procedures [62,63]. SCS–OH (407 mg, 1.204 mmol) was dissolved in a 1:2 mixture of CH_2Cl_2 (5 ml)/CH_3CN (10 ml) and $Pd(PhCN)_2Cl_2$ (462 mg, 1.204 mmol) was then added in one portion. The dark orange mixture was stirred for 30 min under argon, at which point $AgBF_4$ (470 mg, 3.333 mmol) was added and the solution was stirred for an additional 30 min in the dark. The solvent was then evaporated to dryness under reduced pressure, n-Bu_4NCl (2.0 g, 7.20 mmol) in 20 ml CH_2Cl_2 was then added, and the resulting mixture was stirred under argon for 48 h. The silver salt was removed by passing the orange-red mixture through an alumina column. Crude complex **3** was obtained after solvent removal, which was used for the next step without further purification.

*2.2.2. Synthesis of Pd–Cl 3-(3,5-bis(phenylsulfanylmethy-phenoxy)propyl-trimethoxysilane (**4**)*

Complex **3** (250 mg, 0.528 mmol) was mixed with 3-iodopropyltrimethoxylsilane (150 mg, 0.517 mmol) and Cs_2CO_3 (350 mg, 1.074 mmol) in dry DMF (15 ml). The reaction mixture was stirred at 80 °C for 16 h, and then the DMF was distilled off and the product was extracted into CH_2Cl_2. Recrystallization from CH_2Cl_2/hexane yielded **4** as an orange yellow powder. Yield: 306 mg (93%). ^1H NMR (d^6-DMSO): δ 7.43–7.27 (10H, m, Ph), 6.51 (2H, s, ArH), 4.74 (4H, s, br, SCH_2), 4.09 (2H, m, OCH_2), 3.59 (9H, s, Si(OMe)$_3$), 1.75 (4H, m, CH_2), 0.72 (2H, m, SiCH_2) ppm. Anal. Calcd for $C_{26}H_{31}S_2O_4ClPdSi$: C, 48.67; H, 4.87; S, 10.00. Found: C, 49.14; H, 4.43; S, 9.70.

*2.2.3. Preparation of silica-immobilized precatalyst (**5**)*

Complex **4** (200 mg, 0.329 mmol) was mixed with SBA-15 (1.0 g) in dry toluene (50 ml) and the mixture was stirred at 80 °C for 24 h, at which point the mixture was filtered while hot and washed extensively with THF, acetone, DMSO, and DCM to remove any physiabsorbed complex **4**. The recovered solid was then suspended in 40 ml toluene and excess $HN(SiMe_3)_2$ (0.5 g) was added to cap any remaining surface silanols. The resulting mixture was stirred at room temperature for 24 h and then filtered. Silica-supported **5** was obtained after washing with DCM and THF and dried under high vacuum.

*2.2.4. Synthesis of 4-iodobenzylidene-3-trimethoxyl-silanylpropylamine (**6**)*

4-Iodobenzaldehyde (1.0 g, 4.310 mmol) and 3-aminopropyltrimethoxylsilane (740 mg, 4.134 mmol) were dissolved in anhydrous methanol (20 ml). The amount of 0.5 g of 4 Å molecular sieves was used as water scavenger and the mixture was refluxed for 20 h. After cooling to room temperature, solvent was removed under reduced pressure and the product was extracted with CH_2Cl_2. Subsequently, the mixture was concentrated and the product was recrystallized from CH_2Cl_2 and hexanes. Yield: 1.6 g (95%). ^1H NMR ($CDCl_3$): δ 9.96 (1H, s, CH=N), 7.75 (2H, d, $J = 8.4$ Hz, ArH), 7.45 (2H, d, $J = 8.4$ Hz, ArH), 3.57 (9H, s, Si(OMe)$_3$), 1.81 (4H, m, –CH_2–), 0.71 (2H, m, –CH_2Si) ppm. Anal. Calcd for $C_{13}H_{20}O_3NISi$: C, 39.70; H, 5.13; N, 3.56. Found: C, 39.83; H, 5.01; N, 3.45.

*2.2.5. Preparation of silica-immobilized 4-iodobenzylidene-3-trimethoxylsilanylpropylamine (**7**)*

Complex **6** (1.6 g, 3.89 mmol) was added into a toluene (30 ml) suspension of dry SBA-15 (1.5 g) and the mixture was stirred for 24 h at room temperature. After filtering and washing with hexanes and dichloromethane, the collected solid was mixed with 1.0 g of $HN(SiMe_3)_2$ in toluene (40 ml) and stirred at room temperature overnight. The silica-immobilized **7** was collected by filtration and washed extensively with hexanes and dichloromethane and then dried under high vacuum. FT-Raman: δ 1644 (aromatic C=C), 1585 (C=N), 3056 (aromatic C–H), 2850–2960 (aliphatic C–H), 1053 (Ar–I) cm^{-1}.

*2.2.6. Preparation of polynorbornene-immobilized precatalyst (**8**)*

The polymer-immobilized complex was synthesized in 3 steps following a previously reported procedure [64].

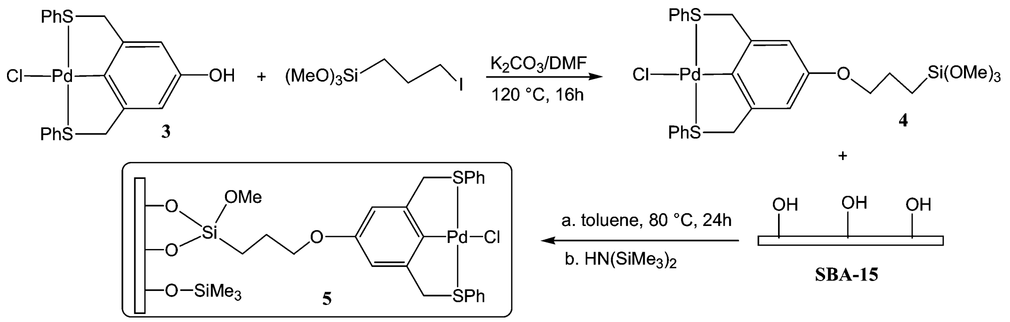
2.3. Catalysis

In a typical Heck reaction, precatalyst **5** (30 mg, 3.6×10^{-3} mmol), iodobenzene (0.56 g, 2.75 mmol), n-butyl acrylate (0.70 g, 5.47 mmol), NEt_3 (0.40 ml, 2.87 mmol), and dodecane (0.4 g, GC internal standard) were mixed in 4 ml DMF in a three-neck round-bottom flask equipped with a condenser and rubber septum. The reaction assembly was then connected to the manifold of a Schlenk line and was gently purged with argon for 10 min before it was sealed. The reaction mixture was then allowed to heat in an oil bath at 120 °C with constant stirring. Aliquots were taken from the reaction mixture periodically, diluted with THF, and conversion was determined by GC chromatography.

3. Results and discussion

3.1. Catalyst synthesis and characterization

Reaction between SCS-pincer palladium(II) complex **3** with 3-iodopropyl-trimethoxylsilane in DMF yields com-



Scheme 2.

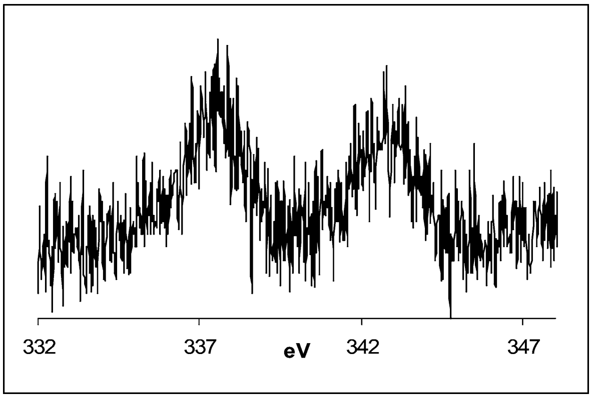


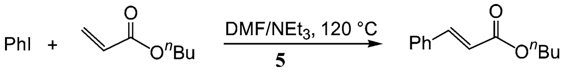
Fig. 1. X-ray photoelectron spectrum of the Pd(II) 3d binding energies in precatalyst **5**.

plex **4** with a $Si(OMe)_3$ end group. The homogeneous SCS pincer palladium(II) complex **4** is covalently immobilized onto mesoporous silica support, e.g., SBA-15, utilizing a reaction between the $–Si(OMe)_3$ group with surface silanols to form Si–O–Si bonds with the concomitant release of methanol (Scheme 2). The remaining accessible surface silanols were capped by reacting at room temperature with excess hexamethyldisilazane. A typical loading for **5** supported on SBA-15 is approximately 0.12 mmol Pd per gram support. The FT-Raman spectrum of **5** (not shown) includes the aromatic C–H stretchings at 3056 and the aliphatic ones at 2850–2987 cm^{-1}, indicating the presence of the pincer ligand. The XPS spectrum (Fig. 1) contains two binding energy peaks at 337 ($3d_{5/2}$) and 343 ($3d_{3/2}$) eV, which is characteristic of a palladium(II) species [65].

3.2. Heck catalysis

3.2.1. Catalytic reactions

The silica-immobilized SCS-type palladium(II) complex **5** was used as a precatalyst for the Mizoroki–Heck coupling of iodobenzene and n-butyl acrylate. The reaction was carried out at 120 °C, using triethylamine as base in DMF as solvent:



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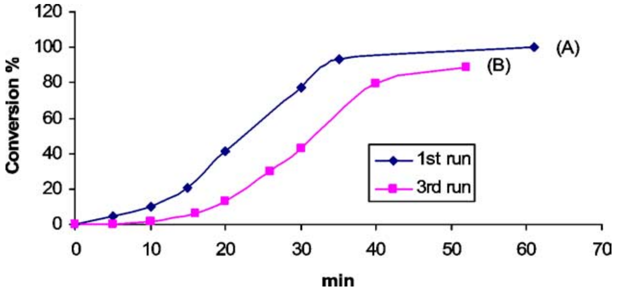

Fig. 2. Conversion of iodobenzene as a function of time for the first (A) and third run (B).

Precatalyst **5** exhibited high activity for the Heck reaction, and high turnover numbers (TON) were obtained (> 700 mol product/mol Pd). The catalyst was recycled three times, and while high yields were achieved even after the third run (Table 1), a longer induction period was observed in the third run. The presence and elongation of the induction period (Fig. 2) between subsequent runs gave the first indication the silica immobilized **5** acts as a precatalyst, with the real active species generated in situ during the reaction [38].

3.2.2. Filtration tests

To demonstrate that all the SCS-pincer Pd(II) complex **5** was covalently bonded to the silica surface and there were no physisorbed species left behind, a filtration/leaching test was performed before each batch of catalyst was used in a reaction. Precatalyst **5** was heated in DMF at 120 °C for 30 min and then filtered while still hot. The filtrate was then kept at 120 °C and iodobenzene, n-butyl acrylate, triethylamine, and GC internal standard n-dodecane were added and the resulting mixture was stirred at 120 °C. GC analysis indicated that only a trace amount of Heck reaction product is produced, with less than 2% conversion of iodobenzene and n-butyl acrylate after 90 min. Compared to the high activity from a regular Heck reaction with precatalyst **5** (Table 1 and Fig. 2), it appears that essentially all the SCS-pincer palladium(II) in complex **5** is covalently bonded to the silica surface.

With many heterogeneous catalysts reported in the literature, there is substantial evidence that leached/dissolved Pd species (colloidal [24] or molecular [25]) are the true active species [9–14]. One way to gather information on the

Table 1
Heck reaction of iodobenzene and *n*-butyl acrylate with **5**[a]

Run No.	Time (h)	Yield[b] (%)	TON	STY[c]
1	1.5	> 99	764	509
2	2	97	733	367
3	3	94	718	239

[a] Reactions were conducted using 30 mg (3.6×10^{-3} mmol) of precatalyst **5**, 5.47 mmol butyl acrylate, 2.87 mmol NEt_3, and 2.75 mmol of iodobenzene in 4 ml of DMF.

[b] GC yield.

[c] Site-time yield (STY) is the TON divided by overall reaction time, which is only a rough approximation of average activity, especially in view of the presence of induction period.

nature of the catalytic site when a solid catalyst is involved is through the use of a simple filtration test during the reaction. For example, a regular Heck reaction performed using precatalyst **5** was interrupted, and the solid was filtered off while hot after 61% conversion of iodobenzene. Subsequently, fresh reagents were added into the filtrate and it was observed that the Heck coupling reaction continued at a rate only slightly slower than the rate prior to the solid removal. When the recovered solid was subjected to identical Heck reaction conditions with new reagents, a substantially slower conversion of the reagents was observed. Furthermore, elemental analysis of the solid before and after the first use indicated that ∼ 17% of the immobilized palladium was lost. This filtration test clearly suggests the presence of active soluble Pd species in solution. However, it does not prove that all the catalysis is solely attributable to soluble species. Since the palladium is covalently bonded to the support before the reaction, one reasonable conclusion is that some of the supported Pd metal is leached out into the solution during the reaction.

3.2.3. *Polyvinylpyridine poisoning*

One of the goals of covalently supporting the SCS-pincer-type palladium(II) complex onto silica supports was that it would allow for the determination of whether the observed reactivity was due to true palladium pincer catalytic species or from palladium species that have been leached/lost into the solution due to pincer ligand decomposition. This is often not possible for palladium catalysts that are just physisorbed on solid supports such as charcoal, since the palladium species will come off the solid during the reaction at high temperature and redeposit back onto the support [28,66]. In addition, for soluble polymer-supported systems [17,18,46–48], it is extremely hard to distinguish any leached soluble Pd species from the polymer-supported moieties as both species can be soluble and complete recovery of low molecular weight soluble polymer from solution may sometimes be impossible.

Since the SCS-pincer palladium(II) complex is covalently bonded onto the insoluble solid support, if during the course of the Heck reaction, some of the palladium species are leached into solution, then both supported and unsupported (leached) palladium metal centers could contribute to the Heck reaction. However, if another insoluble ligand that has the capability to bind strongly to soluble palladium is added during the reaction, one can potentially shut down the activity from the leached, soluble palladium species. By comparing two Heck reactions, one in the presence of the insoluble homogeneous Pd trap and one in the absence of the Pd trap, it is possible to quantify the fraction of the total observed activity that stems from both the supported and the leached palladium species. Pyridines are known to bind strongly to Pd(II) [67]. For this reason, commercially available poly(4-vinylpyridine) (PVPy) (2% cross-linked) was chosen to test this hypothesis. This polymer is insoluble under the reaction conditions. In one experiment, precatalyst **5** is mixed with iodobenzene, *n*-butyl acrylate, triethylamine along with PVPy (molar ratio PVPy:Pd is 100:1) in DMF and heated at 120 °C. GC analysis indicates that less than 1.0% conversion (based on iodobenzene) was obtained even after 3 h. In contrast, as shown in Fig. 3, in the absence of PVPy, nearly quantitative conversion of iodobenzene is observed after only 30–40 min. In another experiment, a Heck reaction was performed under standard conditions and after achieving 34% conversion based on iodobenzene, excess PVPy (∼ 120 eq) was added into the reaction mixture. In this case, GC analysis indicates that the addition of PVPy almost instantaneously quenched the reaction (Fig. 3). The fact that PVPy suppresses the activity of precatalyst **5** strongly suggests that the Heck activity from complex **5** comes from leached/unsupported Pd that is soluble in DMF, since the probability for a high molecular weight insoluble polymer to interact with the SCS-pincer palladium metal centers that are immobilized inside the mesoporous channels of the SBA-15 is negligible. Thus, there is no evidence for catalysis by SCS-pincer Pd under the conditions reported here.

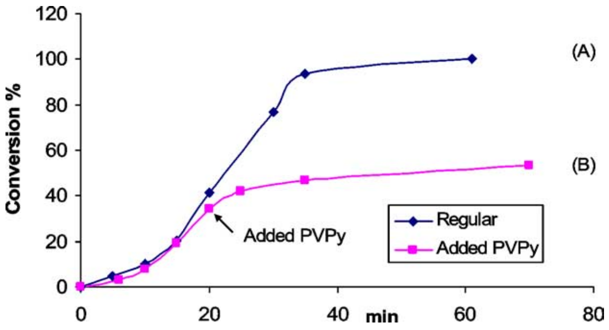

Fig. 3. Conversion of iodobenzene as a function of time under standard conditions (A) and in the presence of 100 eq of PVPy added after 20 min (B).

Furthermore, the above results indicate that the true catalytic species may in fact be homogeneous molecular Pd, as it is difficult to envision how insoluble PVPy could completely poison a reaction that is occurring on a nanoparticle surface.[3] Indeed, as the pincer complex decomposes, molec-

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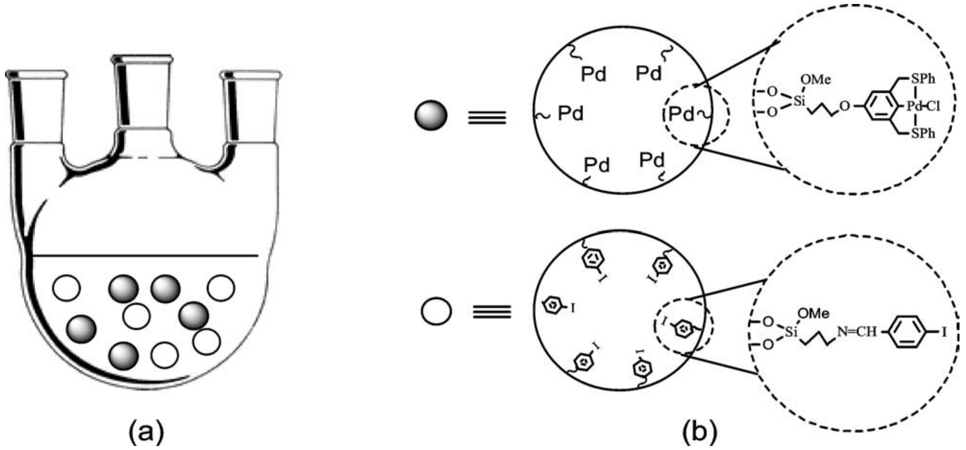
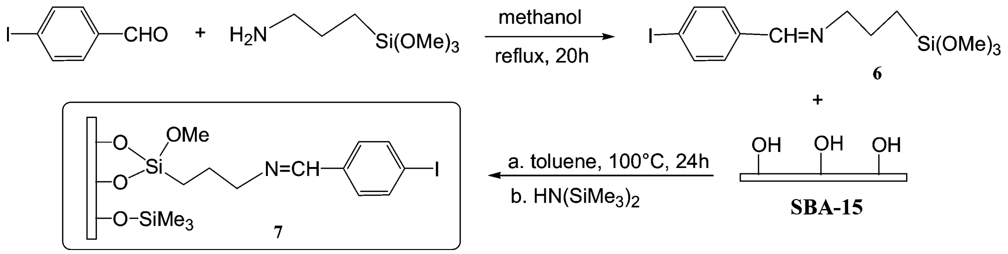
[3] This assumes that for studies involving Pd nanoparticles, it is the nanoparticle surface that is the catalyst. This conclusion is reached in sev-



Scheme 3. Schematic drawing of the three-phase test. Solid and hollow balls represent silica-immobilized pincer-Pd(II) precatalyst and silica-immobilized iodobenzene analogue, respectively.



Scheme 4.

ular Pd species are liberated that could act as the true catalyst or they could aggregate into soluble colloids that could act as the catalyst. A useful control experiment is to prepare preformed stabilized Pd(0) colloids and utilize these in the Heck reaction[4] both in the presence and absence of PVPy. Four otherwise identical Heck reactions (Pd, 2.2×10^{-3} mmol; butyl acrylate, 1.8 mmol; iodobenzene, 0.9 mmol; NEt_3, 1.0 mmol; and internal GC standard) were carried out, one in the absence of PVPy and others with 1, 30, and 100 eq of PVPy relative to Pd metal. Each reaction mixture was kept at 120 °C under constant stirring and after 70 min, GC analyses indicated conversions of iodobenzene were 95, 95, 12, and 8%, respectively. Closer observation of the kinetics of the latter experiment indicates that the reaction proceeds quickly to 8% conversion in the first few minutes of the reaction and then the reaction proceeds no further. This observation indicates that PVPy is not capable of completely poisoning a system with a nanoparticle precatalyst under the conditions used here, although a large excess of PVPy can eventually shut down the catalytic productivity. These results neither conclusively prove nor rule out either catalysis by the surface of Pd nanoparticles or molecular Pd(0) species, as the stoichiometry of poisons on nanoparticle surfaces can be a complex issue [70].

Nonetheless, the above results clearly demonstrate that soluble Pd species are the true catalysts in the Mizoroki–Heck reaction using a silica-supported SCS-pincer Pd precatalyst. However, the nature of the soluble Pd species is still unknown.

3.2.4. Three-phase test

Although the above results argue strongly for homogeneous catalysis, a more convincingly set of experiments to support this hypothesis is the use of a three-phase test. The "three-phase" test, proposed by Rebek and co-workers [71,72] and used by Davies et al. [66] and others [28,73,74], entails anchoring one of the reagents onto a solid in addition to using a separate solid-supported catalyst (Scheme 3). In this way, if the Heck reactivity completely comes from the supported metal center, no transformation should be observed for the anchored reagent, as the two solids cannot access each other on the molecular level. In contrast, if during the course of the reaction some active metal species are leached into the solution, the anchored reagent will be converted to some degree. With this in mind, we prepared a supported analogue of iodobenzene that is covalently immobilized onto

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eral studies, although to the best of our knowledge it has not been conclusively shown that catalysis by molecular Pd species that leach from the nanoparticles (as in cases where supported Pd metal is used [13,26]) can be ruled out. Pd nanoparticles immobilized on PVPy [68] or polyvinylpyrrolidone (PVP) [24,69] spheres have been used as Heck catalysts and in these cases, the nanoparticles are implied to be the catalysts.

[4] PVP–palladium nanoparticles were synthesized according to a literature method [69]. The nanoparticles were isolated by evaporation of the solvent followed by washing with water and ethanol and then dried under high vacuum.

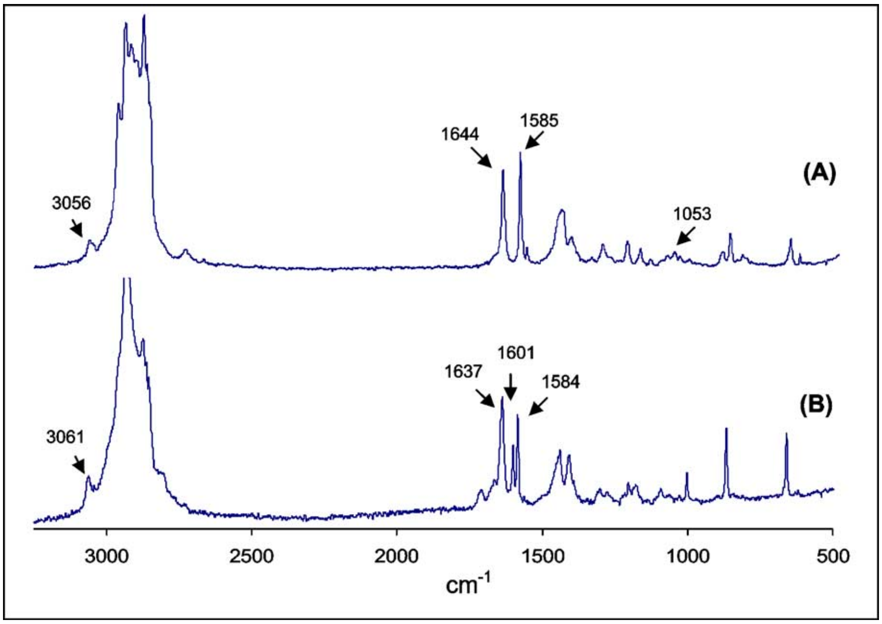
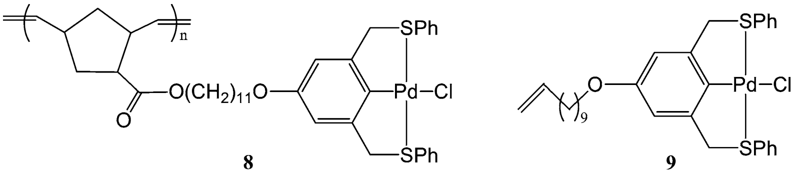


Fig. 4. FT-Raman spectra of **7** (A) and a mixture of **7**, the used precatalyst **5**, and the Heck coupling product (B).



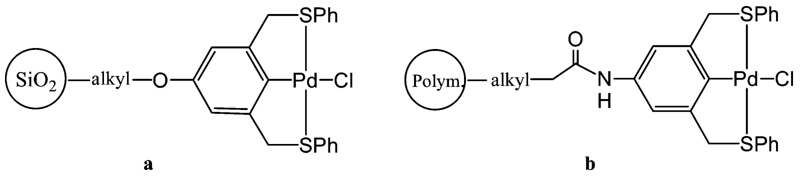
Scheme 5.

the silica surface (Scheme 4). Leaching tests indicated that the immobilized iodobenzene in complex **7** is all covalently bonded to the silica surface and FT-Raman investigations allow for identification of all the key bands of the supported organic (vide infra).

When the Heck reaction of n-butyl acrylate (1.56 mmol) and **7** (400 mg) using complex **5** (37 mg) as catalyst is performed with NEt_3 as base in DMF, GC analysis indicated that after 3.5 h, butyl acrylate conversion was $\sim$ 12%, corresponding to $\sim$ 59% conversion of the anchored iodobenzene. The FT-Raman spectrum of the recovered solids shows an extra Raman band at 1601 cm^{-1}, characteristic of C=O stretch of the coupling product, and decreased intensity of the Ar–I stretch at 1053 cm^{-1}, indicative of the partial conversion of **7** to the coupling product. Another new peak at 1637 cm^{-1} and its shoulders are most likely due to the overlap from the C=C stretch of the acrylate in the coupling product and the aromatic C=C stretches (the coupling product and unreacted **7**). We were not able to conclusively attribute any bands associated with the immobilized precatalyst **5** in Fig. 4B, since **5** accounted for less than 10% in the recovered solid mixture. The successful coupling reaction between n-butyl acrylate and anchored iodobenzene **7** clearly indicates the presence of active soluble palladium species, in agreement with the more traditional catalytic experiments described above.

3.2.5. *Polymer-supported catalyst*

The results described so far indicate that a soluble Pd species is responsible for the Heck catalysis with the silica-supported system. However, it is unclear whether the leached species result from pincer ligand–Pd bond rupture or via Si–O–Si bond rupture to liberate a free Pd pincer complex. To probe this, catalysis by polynorbornene-immobilized SCS–Pd pincer species can be considered. Polynorbornene-immobilized catalyst (**8**) does not contain any Si–O–Si linkages between the pincer complex and the support (Scheme 5). Precatalysts of this type have been previously shown to be capable of promoting the Heck reaction under similar conditions [75]. However, in the presence of 100 eq of PVPy, Heck catalysis was completely extinguished. The reaction was monitored every 5 min for 1 h, then every 8 h for 48 h. No activity was observed. The polynorbornene-based polymer is soluble under the conditions of the reaction; thus, it may be feasible for the nonsoluble PVPy to interact with some of the supported complexes and poison activity associated with them. However, a complete loss of activity over prolonged periods of time is likely not consistent with activity from immobilized sites, as extinguishing all sites with the insoluble polymer is statistically unlikely unless the active species is homogeneous. Thus, these observations are consistent with Pd leaching through decomposition of the ligand–Pd bonds.



Scheme 6.

Hence, the leaching observed with the silica-supported catalysts is likely also attributable to a similar leaching mechanism.

3.2.6. Mercury poisoning test

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 [74,76,77]. Hg(0) is especially effective in poisoning Pt, Pd, and Ni metals in forming an amalgam [76]. 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. When a Heck reaction is performed in the presence of excess Hg(0) using precatalyst **5**, no activity is observed even after 2 h. This provides evidence that the SCS-pincer-type Pd(II) precatalyst decomposes under reaction conditions to form soluble Pd(0) species and that Hg(0) interactions with these Pd(0) moieties completely kill the reaction. In a similar experiment, in the presence of excess Hg(0), the homogeneous SCS-pincer Pd(II) complex **9** also showed no Heck reactivity. This is consistent with a breakdown of pincer ligand–Pd bonds to liberate Pd(0) species.

3.2.7. Insights into the Heck reaction mechanism

Although a catalytic mechanism involving Pd(0) and Pd(II) intermediates is well-established with a number of different precatalysts, the real nature of the active species in SCS-pincer Pd catalysis is still not clear. Indeed, the controversial issue of a Pd(II) and Pd(IV) intermediacy in phosphine-based palladium-catalyzed Heck reactions attracted much research interest and is still under debate [31, 37,78–81]. However, there is still no definitive evidence in the literature to support this mechanism. The results from our investigation indicate that unsupported Pd species have been leached into the solution (perhaps the cause of the induction period), and the supported Pd metal center (those still attached to the pincer ligand) is not active for the Heck coupling reaction. Furthermore, the Hg test and polymer-supported catalytic results show that the leached species are very likely decomposition products of the pincer complex and not simply intact pincer species leached due to Si–O–Si bond rupture. These results support a catalytic mechanism involving Pd(0) and Pd(II) intermediates.

Soluble colloidal palladium nanoparticles often impart a reddish-orange tint in DMF [42]. The same color change from an initial light yellow to reddish is also observed during a Heck reaction using the homogeneous SCS-pincer complex **9**. To ascertain whether Pd nanoparticles exist in solution after reaction, TEMs of both the reaction solution and the catalyst precursor were obtained. The images verified the presence of nanoparticles in the solution (particle sizes ∼ 2–4 nm) but not in the catalyst precursor. This supports the notion that palladium comes off the pincer ligand during the induction period and forms soluble Pd species. How Pd(0) is generated and the nature of the soluble *active* palladium species are still unknown. In the case of some NC-palladacycle precatalysts, Beletskaya et al. observed that prereduction of Pd(II) with a simultaneous disassembly of a palladacycle could be effected by the olefin in a non-catalytic Heck reaction [38,82]. In another study, Biffis et al. demonstrated that under Heck conditions, heterogeneous palladium metal catalysts underwent significant leaching in the presence of aryl halides [9]. In order to ascertain which agent(s) caused the metal leaching in the case of our silica immobilized precatalyst **5**, several control experiments were performed. Precatalyst **5** was allowed to contact one or two reagents in DMF at 120 °C for 5–30 min, and the reaction mixture was filtered while hot under argon and any missing reagents were then added into the filtrate. The resulting solid-free mixture was allowed to stir at 120 °C and kinetics was monitored through GC analysis. We found that neither iodobenzene nor NEt_3 alone caused any palladium leaching, while a combination of both caused significant metal leaching. For example, **5** (3.6×10^{-3} mmol) was mixed with NEt_3 (2.87 mmol) and iodobenzene (2.75 mmol) in DMF (5 ml) and allowed to stir at 120 °C for 30 min, at which point, the solid was filtered off under argon. When *n*-butyl acrylate (5.47 mmol) was added into the filtrate and the resulting mixture was allowed to stir at 120 °C, GC analysis indicated a conversion (based on iodobenzene) of 99% after 93 min. Moderate metal leaching was also observed with a combination of NEt_3 and *n*-butyl acrylate. While palladium leaching in the presence of iodobenzene/NEt_3 might be the direct consequence of the oxidative addition of the organic halide to the metal center [9,66,83], the leaching mechanism from *n*-butyl acrylate/NEt_3 is less straightforward. The real nature of the active leached species, whether in the form of colloidal nanoparticles/clusters and/or molecular palladium species, is still unclear. Further examination is warranted.

3.2.8. Nature of the true catalytic species

All of the experiments here, when taken together, support the existence of soluble, Pd(0) species as homogeneous catalysts. There is no evidence for catalysis by Pd–SCS species under the conditions evaluated here. In considering catalysis by soluble Pd(0) colloids or Pd(0) molecular species, the evidence here supports catalysis by molecular Pd(0) species that are present in solution in equilibrium with Pd(0) colloids. The color of the solution (from orange to deep red) is consistent with the presence of Pd colloids. Furthermore, Pd nanoparticles have been observed in solution after reaction by TEM. In addition, after all of the substrate has been consumed, Pd black is sometimes observed to form when the reaction is carried out under argon. Prior to this, however, the solution appears homogeneous. Although catalysis by Pd colloids cannot be conclusively ruled out, the observation that the *insoluble* PVPy polymer effectively extinguishes reactions (essentially completely) may be more consistent with catalysis by molecular species than with catalysis mediated by the surface of Pd colloids [24,68,69]. Poisoning by Hg(0) is believed to be consistent with either catalysis by "naked" molecular Pd(0) or Pd(0) colloids. If molecular Pd(0) species are the true catalysts, these results are consistent with those of de Vries et al. [25], Kohler and co-workers [12,13], and Arai and co-workers [10,11] who have found that catalysis by molecular Pd(0) is likely when starting with $Pd(OAc)_2$ or supported Pd(0) as precatalyst sources.

Thus, in many cases where Heck catalysis is reported by "recyclable", "recoverable" immobilized molecular catalysts, it is highly likely that homogeneous species account for some or all of the observed catalytic productivity. Especially in cases where the only test for catalyst stability that was carried out is the capability to recover and reuse the catalyst (and where reaction yields are reported instead of kinetics), one needs to exercise caution in labeling the catalysts as truly recoverable and recyclable systems [56,84–86]. In many cases, it is possible that these are simply recoverable precatalyst sources that leach active species into solution in each use. For example, with the catalysts described here, the immobilized Pd complex is simply a recoverable Pd reservoir. After one reaction, 17% of the Pd is lost into the solution as active Pd(0) species. Furthermore, XPS spectra of the used catalyst still show the characteristic peaks for Pd(II) species, with no additional peaks for Pd(0) or Pd(IV) species. Thus, 83% of the Pd precatalyst sites remain after one use and this solid can be reused until all of the Pd is depleted from the solid. Hence, without the crucial control and poisoning studies utilized here (and outlined by Finke and co-workers [74] and others [28,66,73]), one cannot readily conclude that a recyclable and recoverable catalyst is in hand.

3.2.9. Implications for Heck catalysis with other pincer complexes

Other studies of immobilized PCP [56], SCS [17,18,46–48], and NCN [49] Pd pincer complexes have implied that these complexes are stable under reaction conditions and thus the supported catalysts are recyclable. It is interesting that rather subtle changes of ligand structure may drastically change the behavior of these complexes, even changes that are a substantial distance away from the Pd–ligand bonds. For example, within the SCS–Pd pincer family, two types of catalysts have been prepared as shown in Scheme 6. The Pd–SCS–O pincer complexes (ether linkage to the support tether, Scheme 6a) that are described here have been conclusively shown to decompose to catalytically active Pd(0). This observation is in line with earlier work by Bergbreiter et al. on the polymer supported systems, where traces of Pd black were observed with similar complexes [48]. Surprisingly, simply changing the linkage to the support tether to an amide may drastically alter the behavior of the complexes. These Pd–SCS–N complexes (Scheme 6b) are claimed to be stable under reaction conditions, yielding recoverable, recyclable catalysts [17,18,46–48]. Additional studies of silica-supported versions of this Pd–SCS–N system as well as Pd–PCP systems are currently underway in our laboratories.

4. Conclusions

In summary, SCS-pincer-type Pd(II) complexes have been successfully immobilized onto polymeric and mesoporous silica supports through covalent bonds. The supported pincer Pd(II) complexes were utilized as precatalysts in the Mizoroki–Heck reaction. It is demonstrated that there is no evidence for any heterogeneous catalysis and all the Heck activity comes from leached soluble palladium species that likely result from decomposition of the pincer ligand. Further studies concerning the nature of these leached species and efforts toward the development of stable solid catalyst systems are underway.

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