

"Click" Immobilization of Organometallic Pincer Catalysts for C-C Coupling Reactions

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Model systems for the simple, high-yielding, efficient "click" immobilization of homogeneous pincer catalysts are demonstrated. We present the synthesis of azide- and isocyanate-functionalized high pore volume, low surface area silica materials. Both *para*-ethynyl-functionalized palladium and platinum pincer organometallics (pincer = $[C_6H_3(CH_2NMe_2)_2-2,6]^-$) were coupled with azidofunctionalized silica material, yielding the corresponding tethered complexes in high yields with no complex degradation. Analogous para-alcohol-functionalized palladium and platinum pincer complexes were coupled with isocyanate-functionalized silica material to vield immobilized organometallics in high yields. The acquired immobilized organometallic pincer complexes were characterized using various techniques (solid-state IR and NMR, elemental content analysis, surface area measurements). Palladium-containing materials were applied as Lewis acid catalysts in the double Michael addition reaction between ethyl cyanoacetate and methyl vinyl ketone. When measured on a per palladium site basis, the novel materials were found to be as active as the homogeneous forms of the catalyst. This led to the discovery that one of the support materials, with no palladium organometallic units, however, with linker triazole groups present, was also an active catalyst, albeit with slightly diminished activity compared to the palladium-containing material. The palladiumcontaining materials were also applied in allylic stannylation catalysis and were found to be active catalysts, approximately three times slower than the homogeneous catalysts when measured on a per palladium site basis. The support material was not found to be an active catalyst in this reaction. The immobilized palladium catalysts have been applied sequentially for the two-step conversion of an allyl chloride to an allylic alkylation product.

Introduction

The process of manufacturing fine chemicals has consistently been a coproducer of environmentally damaging solvent and non-natural chemical waste.¹ Interest in the sustained development of homogeneous catalysts for fine chemical production has led to the opinion that a method for heterogenizing these catalysts must be developed and brought to the industrial arena.² Several methods for heterogenization of homogeneous catalysts have been explored that are mainly based on inorganic support systems,³ dendrimers,⁴ or functionalized organic polymers.⁵ In addition, significant effort has been expended to develop catalysts for biphasic reaction systems.⁶ It is generally acknowledged that

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covalent immobilization of ligands and complexes on an inorganic support gives the best recycling results. However, covalent immobilization of any organic species on an inorganic support requires multistep reaction procedures that often fail at the last hurdle, i.e., the reaction of functionalized ligand or complex with the inorganic support. Failure comes either through ligand/complex decomposition due to the properties of the inorganic support or due to the relatively extreme conditions required to immobilize. A simple method to couple a functionalized inorganic material with a functionalized ready-to-use catalyst has, in our opinion, not yet been demonstrated.

An area of organic chemistry that has gained precedence in recent years is the so-called "click" reaction chemistry.⁷ This broad area of organic synthesis incorporates any reaction that has high atom efficiency, low byproduct levels, and high yields. The ultimate "click" reaction is defined by a complete conversion of all starting materials, no side-product formation, and relatively mild reaction conditions. The most widely used reaction under the "click" heading is the copper-(I)-catalyzed Huisgens 1,3-dipolar cycloaddition reaction between an alkyne and an azide, yielding a single isomer of a 1,2,3-triazole, the 1,4-isomer.⁷ Recent work has shown the application of "click" chemistry for the tethering of molecules to both organic and inorganic polymeric supports. Biofunctionalization of silica supports by "click" tethering has been demonstrated.8 "Click" chemistry has also been applied for the immobilization of Cinchona alkaloid derivatives on silica9 and also to immobilize coordination complexes on SAM-coated gold surfaces,¹⁰ as well as to organic polymeric supports.¹¹ The latter has shown the application of the formed functionalized triazole bound to a dendritic support as a ligand in copper-catalyzed benzovlation reactions. Chiral pyrrole derivatives have been "click" immobilized on polystyrene for organic catalysis in water.¹² Most recently the controlled loading of copper catalysts by "click" tethering on silica has been demonstrated.¹³

The so-called pincer organometallic complexes have been utilized by our group to demonstrate a range of techniques for catalyst recycling. A pincer organometallic is generally described as a terdentate ligand bound to a metal center via one sigma and two dative bonds.¹⁴ Previous work has demonstrated the application of pincer metal complexes of the general formula $[M(C_6H_3(CH_2X)_2-2,6)]$ (X = SR,¹⁵

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NR₂,¹⁴ PR₂¹⁶) immobilized on dendritic,¹⁷ organic polymeric,¹⁸ and inorganic supports.¹⁹ Pincer metal complexes have been applied in a wide range of catalytic reactions: aldol condensation.²⁰ double Michael addition (this reaction is often used to demonstrate the feasibility of a certain immobilization technique),²¹ Kharasch addition,²² transfer hydrogenation,²³ transfer dehydrogenation,²⁴ and recently allylic stannylation²⁵ and allylic alkylation reactions.²⁶ This latest discovery, where pincer palladium and platinum complexes can be applied in the activation and coupling of allylic substrates, is one of the most promising catalytic applications of pincer palladium species because of the high yields observed. Furthermore, this work has demonstrated the ability of various forms of the pincer ligand with palladium to be active catalysts in cascade processes. For example, the conversion of cinnamyl chloride to cinnamyl stannane followed by reaction with an aldehyde shows a simple onepot process for allylic alkylation of otherwise unreactive substrates.

In this paper we demonstrate the development of novel azide- and isocyanate-functionalized silica materials. These functionalized materials react with ethynyl groups or nucleophiles, respectively, yielding tethered organic moieties with no side products and complete conversion of the respective silica-bound functionality. This so-called "click" immobilization has been demonstrated for a range of organometallic pincer palladium and platinum complexes. The developed materials have been applied in the double Michael addition and allylic stannylation reactions showing high yields and activities, which are, unexpectedly, not substantially diminished compared to the homogeneous catalysts. The roles of the support material and linkers have been investigated, and it was found that the support/tether can have a significant effect on the catalytic reactions. The recycling of the catalytic materials has been studied and shows that the highly stable organometallic catalysts are stable to multiple recycles. It is demonstrated that catalyst immobilization can be a simple, high-yielding process, without complex degradation, and that catalysts immobilized

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Scheme 1. Synthesis of Azide- and Isocyanate-Functionalized Materials 1 and 2



using "click" techniques can be recycled. The "click" immobilization technique allows for simple, one-step, lab shelf to reaction vessel application of functionalized homogeneous catalysts, in a heterogeneous manner.

Results and Discussion

Synthesis. Novel materials for high-yielding, highly atom efficient "click" immobilization of homogeneous catalysts were synthesized (Scheme 1). The conditions for the synthesis of chloro- or amino-propyl-functionalized silica are relatively harsh, with relatively high temperatures required, in the presence of a large concentration of acidic silanol groups. Obviously these conditions could be too extreme for the immobilization of a labile coordination complex or an acid-sensitive species. Therefore, one would prefer to be able to react a functionalized complex with an appropriate support under mild conditions, which are compatible with the precious complex and do not result in the decomposition thereof. The chloro- and amino-propyl-functionalized silica's were reacted with hexamethydisilazine to cap all remaining silanol groups. High pore volume, low surface area silica was used in this study, because we wish to focus on organic moieties bound only at easily accessible sites in the silica. We hope to avoid mass transport limitations and effects on the kinetics of catalytic reactions that come as a result of highly porous silica.

The conversion of chloro- and amino-propyl groups, bound to silica, to active functionalities was successful using standard practices for the synthesis of azides²⁷ and isocyanates.²⁸ The reaction of alkyl halides with sodium azide is a high-yielding reaction with only NaCl as a byproduct. Chloropropyl-functionalized silica was reacted with a large excess of NaN₃ (with respect to [wrt] Cl), yielding material **1**, which could be isolated and purified by simple filtration and washing with water and acetone. Likewise, the synthesis of isocyanates from alkyl amines is a high-yielding reaction with byproduct that can easily be removed. Material **2** was synthesized by reaction of amino-functionalized silica with a large excess of triphosgene (wrt NH₂) and subsequently isolated and purified, by simple filtration and washing with (nucleophile-free) organic solvents. These synthetic techniques have been chosen because they ensure all chloro or amino functionalities are converted to the desired azide and isocyanate, respectively.

Reaction of 1 with an excess of ethynylbenzene in the presence of a catalytic amount of [Cu(MeCN)₄]PF₆ led to complete conversion of all azide groups (as determined by IR spectroscopy, vide infra). However, after several washing steps and a Soxhlet extraction, the isolated material was blue in color. This suggests the presence of remnant copper(II) species on the material. Several attempts to remove these species from the silica surface were made using aqueous ammonium halide solutions, highly acidic/basic solutions, and solutions containing EDTA. However, none of these procedures showed complete removal of the copper from the material. Recent work in our group has shown the application of a Cu(I) thiolate catalyst [CuSC₆H₄(CH₂NMe₂)-2]₃ (5 mol %) for the Huisgen 1,3-dipolar cycloaddition of an alkyne with an azide.²⁹ When this catalyst was used for the reaction of 1 with ethynylbenzene, the silica material showed no visual signs of copper remnants. Furthermore, elemental content analysis showed there was no copper present. Material 1 was subsequently reacted with ethynyl-functionalized palladium and platinum organometallic pincer species,³⁰ yielding immobilized complexes that could be applied in catalysis (Scheme 2 top). The Cu(I) thiolate catalyst (5 mol % wrt ethynyl compound) was used again in this immobilization procedure. In both cases no signs of palladium or platinum complex decomposition were observed. It was also found that the palladium and platinum complexes did not catalyze the Huisgen 1,3-dipolar cycloaddition reaction themselves and that the Cu(I) thiolate catalyst was essential for the reaction to occur at an efficient rate. Upon the completion of the reactions, it was sometimes observed that not all azide had reacted (as determined by IR spectroscopy, vide infra), so fresh solvent and Cu(I) thiolate catalyst were

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Scheme 2. (Top) "Click" Huisgen 1,3-Dipolar Cycloaddition of an Alkyne and an Azide for the Immobilization of Pd and Pt Pincer Organometallics; (Bottom) "Click" Nucleophilic Attack of an Alcohol on Isocyanate for Immobilization of Pd and Pt Pincer Organometallics



added with ethynylbenzene to "cap" any remaining azide groups.

The reaction of material 2 with various nucleophile-functionalized organic species was also analyzed (Scheme 2 bottom). The reaction of 2 with hydroxymethylbenzene (benzyl alcohol) in benzene proceeds at room temperature with complete conversion of all isocyanate groups. The reaction of hydroxyl-functionalized organometallics with isocyanate groups, as previously shown in our group," requires a large excess of NEt₃, with a catalytic amount of N,N-dimethyl-4-pyridine amine (DMAP) in refluxing dichloromethane to ensure conversion of all isocyanate groups. Materials 7 and 8 were produced under these conditions. The fact that more forcing conditions (excess NEt₃, higher temperatures) were required is very important for any future work. Much less extreme conditions are required to couple alkyl nucleophiles than to couple aromatic nucleophiles, and hence the "click" coupling is a step easier and more efficient. Any remaining isocyanate groups on the silica surface were capped by addition of hydroxymethylbenzene to the solution. The quantity of remnant isocyanate groups for materials 7 and 8 and azide groups for materials 4 and 5 could not be quantified easily, and thus after any immobilization procedure excess hydroxymethylbenzene or ethynylbenzene was always added to ensure capping of all remnant functionalities.

Previous work in our group has shown models for materials 7 and 8.¹⁹ Here we report the synthesis of compounds 9 and 10, *para*-triazolo-functionalized pincer palladium and platinum organometallics (Figure 1). These compounds are synthesized in a similar manner to materials 4 and 5; however azidomethylbenzene (benzyl azide) is the coupling agent instead of silica-bound propyl azide. In both cases the reactions are high yielding.

Elemental Analysis. Elemental content analysis has been used to characterize materials 3-8. Nitrogen content analysis gives us indications how the synthetic procedures that have been carried out on the materials affect the substituents present. Carbon, silicon, and oxygen analysis gives little

information because they are present in large excess with respect to the organometallic species (C as TMS capping groups, Si and O as polymeric support). Material 1 shows no Cl content, suggesting that all chloropropyl groups have been substituted by azide. The nitrogen loading is 1.39% of all material. Reaction of 1 with ethynylbenzene (for 3) showed little change in the nitrogen content (1.35%) and a marked increase in carbon content, as expected (3.49% to 5.56%). Reaction of ethynyl-functionalized palladium and platinum complexes showed an increase in nitrogen content, as would be expected (ligands contain N). The "loading" of catalytic sites was determined by measuring the palladium and platinum elemental content (4, Pd = 0.52%; 5, Pt =0.45%). The metal to nitrogen content comparisons show that not all surface triazole groups are tethered to a metal pincer complex, and in fact there is a quantity of "free" triazole groups present as a result of capping any remnant azide functionalities. The nitrogen loading is in fact five times as much as would be expected if all azide groups had reacted to yield an immobilized pincer complex (expected N:Pd 5:1, observed 26:1).

Isocyanate-functionalized material **2** gave similar results. The nitrogen loading was found to be 0.77% of the total mass. The introduction of a pincer organometallic functionality showed a marked increase in nitrogen content, as would be expected for NCN-pincer metal complexes. Again the loading of catalytic material was measured using metal content analysis (Pd **7**, 0.26%; Pt **8**, 0.79%).

Surface Area Measurements. BET surface area measurements were used to analyze the effects of carrying out organic synthetic techniques on the silica material used for the preparation of materials 1 and 2^{31} Both materials showed similar results, demonstrating that there is little difference in the effect of the organic synthesis on the nature of the support material. The surface area of the starting material was approximately 218 m²/g, which compares favorably with the data obtained for materials 1 and 2. Both materials showed a surface area of 208 m²/g. This is an expected decrease, which comes with the coupling of organic moieties to the silica surface, thus decreasing the surface area. The pore diameter and volume measurements also gave valuable information about catalyst site accessibility. We set out to

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Figure 1. Triazolo-functionalized pincer palladium (9) and platinum (10) complexes as model compounds for materials 4 and 5.



Figure 2. IR DRIFT difference spectra of **1** (azide) and **2** (isocyanate) minus starting SiO₂.

wavenumber cm-1

immobilize catalysts without having influences from the support material. This is reflected in the observed pore volumes for materials **1** and **2** versus the starting material. On loading the silica material with the tethering functionality, the pore volume drops minimally. The observed large pore volumes ($\sim 1 \text{ cm}^3/\text{g}$) and the observed pore size (16–17 nm) mean it is highly unlikely that the support has much influence on the kinetics (mass transport) of the catalytic reactions.

By combining the nitrogen content analysis results of materials 1 and 2 with the BET surface area results we can get an indication of the "area" per a single catalytic site and the proximity of catalytic sites to each other. This relies on the assumption that all azide/isocyanate sites are available for reaction with functionalized organometallic species and the entire surface of the material is accessible to the organic moieties used to functionalize the material. With material 1 the nitrogen content is 1.39% of the total loading, which gives $4.76 \times 10^{-6} \text{ mol/m}^2$ nitrogen loading. This can be



Figure 3. IR DRIFT difference spectra of materials 5 and 8, minus starting materials 1 and 2, respectively.

Table 1. BET Surface Area, Pore Volume, and Pore Size Measurements of Materials 1 and 2

material	surface area (m^2/g)	pore volume (cm $^3/g$)	pore size (nm)
starting SiO ₂	218.40	1.13	20.61
1	208.20	0.92	17.62
2	208.09	0.86	16.47

converted to functionality loading by dividing by 3 (three nitrogens for every azide), which gives $1.59 \times 10^{-6} \text{ mol/m}^2$ $(1.59 \times 10^{-26} \text{ mol/Å}^2)$ azide loading. Using Avogadro's constant this gives an approximation that every azide group sits on 104.4 $Å^2$. In the case of material **2** (isocyanate) the nitrogen content is 0.77% of the total material content. This gives 2.64×10^{-26} mol/Å² of nitrogen (and thus isocyanate), leading to an approximation that every isocyanate group sits on 63.0 \AA^2 . Simplifying the calculations even further, we can estimate the "ideal situation" distance between catalytic sites. Assuming that all catalytic sites are randomly distributed on the silica surface, we treat every functionality site as a cylinder lying perpendicular to the silica surface. The estimated radius (r) of the area around a catalytic site could be acquired from πr^2 = area. Therefore, in material 1, the average distance between catalytic sites is equal to 2r, and thus is 11.3 Å, and in material 2 it is 9.0 Å. This appears to be quite a short distance and would suggest interactions between functionalities (and thus catalytic sites) in materials 1 and 2 are likely (and thus also materials 3–8).

Infrared Analysis. DRIFT³² and ATR³³ IR spectroscopy has been utilized to analyze materials 1-8 and complexes 9

⁽³²⁾ DRIFT-IR (diffuse reflectance Fourier transform) is a surface technique that analyzes reflected IR beam from the surface/near surface of the material.

⁽³³⁾ ATR-IR (attenuated total reflection) is a technique whereby transmission of an IR beam through a sample is measured.



Figure 4. ²⁹Si CP-MAS NMR spectra of materials 4 and 7.

and 10. In particular DRIFT difference spectroscopy has been used to analyze what has been "added" and "sub-tracted" from the materials 1-8. DRIFT difference spectra of materials 1 and 2 are depicted in Figure 2 (spectrum of material minus spectrum of unfunctionalized silica).

Azide-functionalized material **1** shows a characteristic $v_{\rm NNN}$ at ~2030 cm⁻¹, while isocyanate-functionalized material **2** shows a characteristic $v_{\rm NCO}$ at ~2276 cm⁻¹. The intensity of the resonances is a valuable characteristic of these materials. Furthermore, the stretches lie in a region of the spectrum that is unlikely to have resonances from other functional groups. This means that reaction of the functionalities can be easily monitored with IR spectroscopy. Both difference spectra show a trough at ~3740 cm⁻¹. This corresponds to where $v_{\rm SiO-H}$ is expected. This means that Si–OH groups have been consumed in the process of converting silica to functionalized materials **1** and **2**. This confirms that triethoxysilyl groups have reacted with surface silanol groups, yielding covalently functionalized materials.

The IR DRIFT difference spectra (from starting material) of materials **3**, **4**, and **5** showed similar and agreeing results (Figure 3, **5** is depicted). In all cases the azide resonance was consumed (trough at 2030 cm⁻¹), and new resonances were observed at ~1450 cm⁻¹. These resonances are not very intense; however, they are the only characteristic resonances of a triazole group. The pincer complex unit itself has no strong IR stretches and are likely masked by the triazole and silica bands. The ATR IR spectra of **9** and **10** show the similarities between materials **4** and **5** and their untethered analogues.

The synthesis of materials 6-8 showed likewise a consumption of isocyanate groups upon reaction of 2 with nucleophile-functionalized moieties. The formed carbamate group has characteristic stretches at ~1650 and 1550 cm⁻¹.³⁴ Figure 3 also shows the IR DRIFT difference spectrum of 8, which clearly depicts the above-mentioned characteristics. The features of this spectrum are comparable to previous reports on carbamate -tethered silica species.³⁵ As mentioned previously, any remnant isocyanate or azide groups on the silica surface are capped by hydroxymethylbenzene or ethy-

Scheme 3. Double Michael Addition between ECA and MVK with Pincer Palladium Complexes



nylbenzene, respectively. The depicted spectra are difference spectra; however the normal DRIFT spectra of materials 3-8 show no azide or isocyanate resonances, indicating all functionalities have reacted.

NMR Analysis. ²⁹Si CP-MAS NMR was applied to analyze the effects of carrying out organic synthetic techniques on silica (²⁹Si spectra of materials 1, 2, 5, and 8 all look similar to those depicted in Figure 4). The ²⁹Si spectrum of organometallic-containing materials 4 and 7 shows us several peaks that indicate different forms of silicon species (Figure 4). Peaks at \sim -101 and -111 ppm are characteristic of Q-type $(Si(O-)_4)$ silicates, which are in the bulk material. Peaks at \sim -58 and -66 ppm are typical of T-type (R-Si- $(O-)_3$) silicates, that is, the silicon bound to the propyl group at the surface of the support. This is a clear indication that the organic moiety is covalently bound to the support. The presence of double peaks in the -60 ppm (T₂ at 58 ppm, T₃ at 66 ppm) region indicates that not all ethoxy groups of 3-chloro- or 3-aminopropyl-1-triethoxysilane have reacted in the grafting process, and in some cases only two (thus nomenclature T_2) of the three have reacted. The single peak at ~13 ppm is typical of M-type (R_3 Si-(O-)) silicates (where R is the methyl group of the trimethylsilyl-capped silanol groups).

Catalysis. Palladium complexes **9** (*para*-triazole) and **11** (*para*-H, parent compound) and palladium-containing materials **4** (*para*-triazole link to SiO_2) and **7** (*para*-carba-mate linker to SiO_2) were applied as Lewis acid catalysts in the double Michael addition between ethyl cyanoacetate (ECA, cyanoacetic acid ethyl ester) and methyl vinyl ketone (MVK, 3-buten-2-one) (Scheme 3). Previous work has

⁽³⁴⁾ Corma, A.; Das, D.; Garcia, H.; Leyva, A. J. Catal. 2005, 229, 332–331.

⁽³⁵⁾ McDonald, A. R.; van Klink, G. P. M.; van Koten, G., submitted work.

Table 2. Reaction Rate Constants and Half-Lives of	Homogeneous Bromo and	Aquo Pincer Palladium	Complexes 9 and 11 (a and b),
NCN-Pincer Palladium-Containing Materials 4 and 7	7, and Organic-Functional	lized Materials 3 and 6 in	n the Double Michael Addition

		homogeneous catalysts		heterogeneous catalytic materials					
complex/material	blank	9(a)	11(a)	9(b)	11(b)	4	7	3	6
k	0.60	5.10	3.75	25	28				
$(\times 10^{-5} \text{s}^{-1})^a$									
$t_{1/2} (\min)^{a,b}$	1925	226	308	46	41	200	380	370	2000
^{<i>a</i>} As measured by p	plotting ln{[E	CA]/{ECA] ₀	} vs time. ^b W	hen [ECA] =	ECA] ₀ /2.				

demonstrated the application of aquo salts of ECE-pincer palladium complexes (E = SR, NR_2 , PR_2) as catalysts for this reaction.³⁶ It was believed that the metal halide complexes were not active catalysts. In this report we show this not to be true. This alleviates the necessity to use silver salts to convert metal halide complexes into aquo complexes before catalysis. With materials 4 and 7 this is very important, because removal of any formed (insoluble) silver salts from the support would be difficult. Recent work in our group has also demonstrated that silver salts are active catalysts in the Lewis acid catalyzed aldol addition reaction.³⁷ This means, to demonstrate the application of immobilized pincer palladium complexes, one should ensure no remnant silver salts are present. Therefore using the metal-halo complex as the precatalyst is an excellent alternative. Table 2 shows the observed rate constants, k, for both the aquo and bromo pincer complexes 9 and 11 and catalytic materials 4 and 7, as well as functionalized support materials 3 and 6. In all cases 100% conversion was observed.

Both types of precursor (bromo or aquo) showed firstorder kinetics. The blank reaction, thus substrates, base, and solvent, showed $t_{1/2} = 1925 \text{ min } (k = 6 \times 10^{-6})$. With the homogeneous catalysts, 9 and 11, the bromo species is an order of magnitude slower in catalytic reactivity than the corresponding aquo complex. This suggests that in the reactions catalyzed by 9(a) and 11(a) competition between the bromide ligand and substrate ligands is resulting in a slower reaction. We did not observe an activation period for either bromo or aquo catalytic precursors.

Materials 4 and 7 were found to be active catalysts in the double Michael addition. Both were applied as the neutral NCN-pincer palladium bromide complex. The activity of the catalytic material (4, $t_{1/2} = 200 \text{ min}; 7, t_{1/2} = 380 \text{ min}, \text{ Table 2}$) was not diminished when compared to the corresponding homogeneous pincer palladium bromide species, 9(a) and 11(a), respectively. This is a remarkable discovery, because in most instances the covalent immobilization of homogeneous catalysts on inorganic supports results in a substantial decrease in catalytic activity. However, when we investigated the reaction kinetics, we found that the reaction did not follow zeroth-, first-, or second-order kinetics in the ECA substrate (MVK was always used in excess). In fact the organometallic-functionalized silica was expected to demonstrate first-order kinetics, as the homogeneous catalyst does.

Figure 5 depicts the plot, for both materials **4** and **7**, of the natural log of starting material (ECA, from ¹H NMR) concentration against time (a straight-line plot would be

expected for a first-order system). It appears that there is an initial high conversion rate, which then slows at a certain point, and a slower, constant reaction rate is observed. Apparently the support, or heterogenization, is having an effect on the reaction rate.

To investigate the effects of the support material and the linker groups to the support on the Lewis acid catalysis, we synthesized materials 3 (triazole-functionalized silica) and 6 (carbamate-functionalized silica) to mimic the immobilized catalysts 4 and 7, respectively. Neither material contains an organometallic pincer catalyst unit, but have a phenyl end group instead. The source of the surprising catalytic results could arise either from Si-O-Si surface species or from either the triazole or carbamate linkers. Surprisingly, material 3 was found to be an active catalyst in the double Michael addition reaction, when used in the same quantities as materials 4 and 7 (3, $t_{1/2} = 370$ min; 6, $t_{1/2} = 2000$ min, Table 2). Material **3** showed a slightly diminished (factor of 2) activity compared to the homogeneous organometallic catalyst 9(a), while material 6 showed activity similar to the blank reaction ($t_{1/2} = 1925 \text{ min}$). These data suggest material 6 is thus not a catalyst in the double Michael reaction. Because material 6 is not an active catalyst, the obvious conclusion to be drawn is that the triazole-functionalized silica material is an active catalyst, and more importantly, the tethered triazole groups themselves are the likely source of catalytic activity. The triazole ring may act as a basic site, with N's -2 and -3 possible bases. The "catalytic" loading of triazole groups in this reaction is calculated to be 7 mol % (50 mg of 3 used, comparable to quantities of materials 4 and 7 in previous experiments; however, materials 4 and 7 are accompanied by 1 mol % Pd loading as well). With this loading, one could also propose that if the triazole group acts as a base, then there are possibly multiple extra basic sites present in the reaction mixture. No reports on the pK_a of the triazole group have been reported to date,38 so the relative strength of the triazole basic sites cannot be commented upon. As material 4 is a better catalyst than material 3, it can be concluded that the palladium organometallic does play a role in the catalyzed reaction. It is possible that a cooperative effect between triazole groups and the pincer palladium unit is allowing for this increase in activity. It must be noted here that catalysts 9(a) and 11(a) show comparable activities. The BET surface area studies in this report show that the organometallic/triazole groups (vide infra azide) on the silica surface are all relatively close to each other and are more than likely able to interact with or assist each other. Previous work in our lab has also found that coordination between a triazole group and an

⁽³⁶⁾ Dijkstra, H. P.; Slagt, M. Q.; McDonald, A. R.; Kruithof, C. A.; Kreiter, R.; Mills, A. M.; Lutz, M.; Spek, A. L.; Klopper, W.; van Klink, G. P. M.; van Koten, G. *Eur. J. Inorg. Chem.* **2003**, *5*, 830–838.

⁽³⁷⁾ Mehendale, N.; Klein Gebbink, R. J. M.; van Koten, G. N. Mehendale Ph.D. Thesis UU, **2007**, Chapter 8.

⁽³⁸⁾ Evans gives the pK_a of free triazole, and its attraction for a proton, which we believe does not give a strong argument for this particular study. Ripin, D. H.; Evans, D. H. *Chem 206*. http://www2. lsdiv.harvard.edu/labs/evans/pdf/evans_pKa_table.pdf.





Figure 5. Plot of $ln(CN/CN_{[0]})$ concentration of ECA over initial concentration versus time for materials 4 and 7.

organometallic pincer complex yields stable coordination complexes.³⁹ Whether these types of interactions are playing a role is uncertain.⁴⁰

Materials 4 and 7 could be reused/recycled by simple filtration of the catalytic mixture and then washing with dichloromethane and subsequent recharging with substrates and base. Material 4 was found to gradually lose catalytic activity over three cycles. With material 7 all three cycles showed half-lives of ~400 min with quantitative yields. No palladium leaching was observed in either material (Table 3). All three recycles showed the same reaction kinetic profile of the first catalysis test (Figure 7). These results clearly indicate that material 7 is the more stable catalytic material, and something is poisoning the catalyst deactivation could be the triazole coordination to any palladium sites on the surface, thus deactivating both possible active sites. Another likely explanation is that product is blocking the active site



Figure 6. Plot of ln(CN/CN[0]) (concentration of starting ECA over initial concentration) versus time for materials 3 and 6.

Table 3. Palladium and Tin Content of Recycled Catalytic Material

reaction	material 4	material '
Pd		
starting value postcatalysis	0.52%	0.26%
Michael	0.58%	0.40%
stannylation	0.60%	0.26%
Sn stannylation	7.64%	

(triazole) on the silica surface and is not easily washed away in the recycling of the catalytic material. In both cases the postcatalysis filtrate solutions were recharged with fresh substrate. However, no catalytic turnovers were seen in either material, demonstrating that no soluble palladium species are present in the reaction solution.

In order to further test the immobilized NCN-pincer palladium complexes, a catalytic reaction was chosen in which any involvement of the support and linker would be unlikely. Accordingly, we selected the allylic stannylation reaction of allyl chloride with hexamethylditin, yielding an allyl-stannane (Scheme 4). ECE-pincer metal complexes have recently been shown to be highly active catalysts in this reaction (ECE = NCN, SCS).²⁵ Material 4 (triazole linker) showed diminished activity compared to its homogeneous counterpart 9(a) (complete conversion within 1 h; material 4 complete conversion in 6 h), while material 7 showed very slow reaction rates (20% conversion after 72 h). Szabo et al. showed that the *para*-substituent plays a significant role in the activity of the catalyst, with previous work showing the para-nitro NCN-pincer palladium species being the most active catalyst for this reaction. In our opinion, the differences in the electron-withdrawing/donating properties

⁽³⁹⁾ Suijkerbuijk, B. M. J. M.; Aerts, B. N. H.; Dijkstra, H. P.; Lutz, M.; Spek, A. L.; van Koten, G.; Klein Gebbink, R. J. M. *Dalton Trans.* **2007**, *13*, 1273–1276.

⁽⁴⁰⁾ An alternative explanation for the high catalytic activity of materials **3**, **4**, and **7** could be that capped silanol groups have become deprotected. Recent work has demonstrated that functionalized amines have been tethered to a silica/zeolite support and the resulting materials were applied in the double Michael addition reaction. However, that work requires that remnant acid sites (uncapped silanol groups) play a role in the catalysis. We have capped all silanol groups to the best of our knowledge, with the hope of avoiding effects from the inorganic support, and therefore we believe this option to be unlikely. Furthermore, postcatalysis DRIFT-IR of the supported catalytic material shows minimal changes in the SiOH region of the spectrum, suggesting the silanol group capping has not been affected. See: Motokura, K.; Tada, M.; Iwasawa, Y. J. Am. Chem. Soc. **2007**, *129*, 9540–9541.



Figure 7. Kinetic plots of recycled catalysts 4 and 7.

Scheme 4. Pincer Palladium-Catalyzed Allylic-Stannylation Reaction



of a triazole group compared to that of a carbamate group are not great enough to cause such a large difference in reaction rates. Material **3** did not catalyze the reaction of cinnamyl chloride with hexamethylditin, showing that the NCN-pincer palladium unit was the active catalyst in the allylic stannylation reaction. However, the triazole group is not likely to be innocent in this reaction either. The reaction taking place on the palladium center may well be affected by the ability of the triazole group to coordinate any tincontaining compounds. It may also be affected by the ability of the triazole group to intermolecularly coordinate with neighboring palladium centers.

Elemental content analysis of catalytic materials 4 and 7 was done postcatalysis to measure how much palladium had leached into the reaction mixture. Minimal changes (within experimental error) were observed in the palladium content of the various catalytic materials (Table 3). This demonstrates that no soluble palladium species are leaching from the silica surface during the catalytic reactions. Furthermore, it emphasizes the stability of the pincer organometallic unit when acting as a Lewis acid catalyst. The tin content was measured for the postcatalysis material 4 and was found to be 7.64%; this corresponds to 3.2×10^{-5} mol present postcatalysis. In a typical catalytic reaction material 4 contains



Figure 8. Recycled material 4 in the allylic stannylation reaction.

 4.8×10^{-5} mol of triazole and 2.3×10^{-5} mol of pincer complex units. It is likely that both palladium stannane and triazole stannane complexes are on the silica surface after allylic stannylation catalysis. The question this leads to is, can triazole ligands achieve stannylation catalysis? The answer is no: material **3** does not catalyze the reactions; neither does an organic molecule containing triazole groups.

Material **4** showed the best catalytic activity in the allylic stannylation reaction and thus was tested in a recycling study (Figure 8). Material **4** could be recycled by centrifugation and decantation of the reaction solution, resulting in isolation of the solid catalytic material. No loss in activity was observed over three recycles of the catalytic material. Quantitative yields were also observed over three cycles, and no Pd(0) was observed. The postcatalysis filtrate showed no turnovers when fresh substrate was added.

Sequential Catalysis. The filtrate, after simple removal of the tethered material 4 by filtration over a glass frit (from the allylic stannylation reaction), was subsequently immediately used without workup (Scheme 5). The formed cinnamyl trimethylstannane was further transformed in an allylic alkylation reaction, using a PCP-pincer palladium chloride catalyst immobilized on silica made previously in our group (carbamate linker to the support, $P = PPh_2$).¹⁹ The stannane was reacted with 4-nitrobenzaldehyde, giving quantitative conversion to the C-C coupled product 12 as a mixture of diastereoisomers under standard conditions reported by Szabo.^{26b} This result gives a proof of principle of cascade catalysis with immobilized catalysts. For example, in the case where two catalysts are incompatible under certain reaction conditions, catalyst immobilization allows one to simply transfer reaction solutions between reaction vessels containing a specific catalytic material. This approach does not require separation of catalysts (economy of solvent use), while the conditions required for catalysis can be optimized for most operations. A key point in this concept is catalyst stability, which is excellent for many ECE-pincer metal catalysts, as demonstrated for NCN-pincer palladium complexes in this report.

Conclusions

Copper(I)-catalyzed 1,3-Huisgens cycloaddition and nucleophilic reaction of an alcohol with an isocyanate have been applied to demonstrate "click" immobilization of pincer palladium and platinum organometallics on silica. Scheme 5. Sequential Allylic-Stannylation/Allylic-Alkylation Using Immobilized NCN-Pd and PCP-Pd Organometallic Complexes



Novel materials for this "click" immobilization have been developed containing both azide and isocyanate functionalities. The use of soluble *ortho*-aminoarenethiolate copper(I) as catalyst ensures that no remnant copper compounds are on the silica surface after immobilization, which is not the case with other copper(I) catalysts.

The synthesized materials were thoroughly characterized using solid-state IR and NMR spectroscopic techniques and elemental content analysis and surface area measurements. The acquired pincer palladium-containing materials were applied in two types of C-C bond-forming reactions. In the Lewis acid catalyzed double Michael addition reaction of methyl vinyl ketone with ethyl cyanoacetate the developed materials showed activity comparable to the homogeneous catalyst. Furthermore, a model system containing only the linkers that connect the pincer organometallic to the support was found to be almost as active as the homogeneous palladium catalyst. This demonstrates the noninnocent role that the linkers can play in the "heterogeneously" catalyzed reaction. Furthermore in the successful allylic stannylation reactions the triazole linker was again found to be noninnocent. Importantly the synthesized materials are found to be easily recycled over numerous cycles, demonstrating the practical feasibility of the presented immobilization technique. Catalyst stability is an important point in the developed systems. Recycling of the immobilized pincer organometallics resulted in no complex decompositions. This is demonstrated in the recycling experiments in the stannylation catalysis section, where there are minimal differences in the kinetic profile of the three subsequent recycling reactions. The recyclability of the materials relies heavily upon the robustness and stability-both thermal and mechanicalthat pincer organometallics provide.

This report shows that simple one-step lab-shelf to reaction vessel procedures can be applied for the application of homogeneous catalysts in a heterogeneous manner. Simple mixing of a support material with a functionalized organometallic yields a ready-to-use catalytic material that can be removed from the reaction vessel postcatalysis, allowing simple workup of products, and for reapplication of the catalytic material on numerous occasions.

Experimental Section

General Considerations. Standard Schlenk procedures under N_2 were carried out throughout. Reagents were used as supplied from Acros BV or Sigma-Aldrich, unless otherwise stated. ¹H,

¹³C, and ³¹P solution NMR was carried out on a Varian Inova 300 spectrometer or a Varian Oxford AS400. CP-MAS NMR was carried out using a Bruker AV 750. Elemental analyses were performed by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr, Germany. MS measurements were carried out on an Applied Biosystems Voyager DE-STR MAL-DI-TOF MS. IR spectra were recorded on a Perkin-Elmer SpectrumOne FT-IR spectrometer. GC analyses were performed on a Perkin-Elmer AutosystemXL gas chromatograph.

Synthesis of 3-Chloropropyl-1-silica. Silica (10 g, BASF bv Nederland, C500-383) and 3-chloropropyl-1-(triethoxy)silane (10 mL, 0.041 mol) were placed in dry toluene (100 mL) and heated at reflux for 24 h. The mixture was filtered hot, then washed with toluene (2×), boiling EtOH (2×), CH₂Cl₂(2×), and pentane (2×), and subsequently dried under vacuum. White powder. IR (DRIFT, difference): v_{SiO-H} 3740 cm⁻¹ (trough).

Synthesis of TMS-capped-3-chloropropyl-1-silica. 3-Chloropropyl-1-silica (5 g) was placed in dry hexanes (50 mL) with hexamethyldisilazane (5 mL, 3.87 g, 0.024 mol), and the mixture was heated at reflux for 24 h. The mixture was filtered hot, then washed with pentane (2×), boiling EtOH (2×), CH₂Cl₂ (2×), and pentane (2×), and subsequently dried under vacuum. White powder. IR (DRIFT, difference): ν_{SiO-H} 3740 cm⁻¹ (trough). Anal. Found: C 5.90, H 1.31, Cl 4.02.

Synthesis of TMS-capped-3-azidopropyl-1-silica, 1. TMScapped-3-chloropropyl-1-silica (5 g) was placed in DMSO (50 mL) with NaN₃ (5 g, 0.077 mol) and stirred at RT for 96 h. The mixture was filtered, then washed with DMSO (2×), water (4×), and acetone (2×), and subsequently dried under vacuum. White powder. IR (DRIFT, difference): $\nu_{\rm NNN}$ 2037 cm⁻¹, $\nu_{\rm SiO-H}$ 3740 cm⁻¹ (trough). Anal. Found: C 3.49, H 1.10, N, 1.39, Cl 0.0.

Synthesis of TMS-capped-3-(4-phenyl-1*H*-1,2,3-triazole)-propyl-1-silica, 3. TMS-capped-3-azidopropyl-1-silica (1 g) was placed in dry degassed toluene with ethynylbenzene (1 mL, 0.009 mol) and 2-[(dimethylamino)methyl]phenylthiolatocopper(I) (0.025 g, 1.1 mmol) and stirred at RT under inert conditions for 72 h. The mixture was filtered, then washed with toluene (2×), EtOH (4×) CH₂Cl₂ (2×), and pentane (2×), and subsequently dried under vacuum. Light brown powder. IR (DRIFT, difference): $v_{triazole}$ 1450–1430 cm⁻¹, v_{NNN} 2025 cm⁻¹ (trough), v_{SiO-H} 3740 cm⁻¹ (trough). Anal. Found: C 5.56, H 1.15, N, 1.35, Cu not detected.

Synthesis of TMS-capped-3-[(4-[2,6-bis](dimethylamino)methyl]-1-palladium(II) bromide-benzene]-1*H*-1,2,3-triazole)]propyl-1-silica, 4. TMS-capped-3-azidopropyl-1-silica (1 g), 4-ethynyl-2,6bis[(dimethylamino)methyl]-1-palladium(II) bromide-benzene (0.052 g, 1.3 mmol), and 2-[(dimethylamino)methyl]phenylthiolatocopper(I) (0.005 g, 0.02 mmol) were placed in a CH₂Cl₂/ CH₃CN (1:1, 30 mL) solution and stirred at RT for 72 h. The mixture was filtered, then washed with CH₂Cl₂ (2×), CH₃CN (2×), and pentane (2×), and subsequently dried under vacuum. Light brown powder. IR (DRIFT, difference): $\nu_{triazole}$ 1450– 1430 cm⁻¹, ν_{NNN} 2027 cm⁻¹ (trough), ν_{SiO-H} 3740 cm⁻¹ (trough). Anal. Found: C 4.60, H 1.10, N, 1.78, Pd 0.52.

Synthesis of TMS-capped-3-[(4-[2,6-bis](dimethylamino)methyl]-1-platinum(II) bromide-benzene]-1*H*-1,2,3-triazole)]propyl-1-silica, 5. TMS-capped-3-azidopropyl-1-silica (1 g), 4-ethynyl-2,6-bis-[(dimethylamino)methyl]-1-platinum(II) bromide-benzene (0.05 g, 1 mmol), and 2-[(dimethylamino)methyl]phenylthiolatocopper(I) (0.005 g, 0.02 mmol) were placed in a CH₂Cl₂/CH₃CN (1:1, 30 mL) solution and stirred at RT for 72 h. The mixture was filtered, then washed with CH₂Cl₂ (2×), CH₃CN (2×), and pentane (2×), and subsequently dried under vacuum. Light yellow powder. IR (DRIFT, difference): $v_{triazole}$ 1450–1430 cm⁻¹ v_{NNN} 2030 cm⁻¹ (trough), v_{SiO-H} 3740 cm⁻¹ (trough). Anal. Found: C 7.75, H 1.50, N, 1.08, Pt 0.45.

Typical Click Reaction Conditions for Synthesis of 9 and 10. Azidomethylbenzene (90 mg, 0.68 mmol) and 4-ethynyl-2,6bis[(dimethylamino)methyl]platinum(II) chloride-benzene (0.20 g, 0.45 mmol) were dissolved in a 1:1 mixture of CH₃CN/CH₂Cl₂ (2 mL), and 2,6-lutidine (78 mL, 0.68 mmol) and [Cu(Me-CN)₄](PF₆) were added. The resulting mixture was stirred at room temperature for 24 h. Next, Et₂O (\sim 2 mL) was added, resulting in a yellow precipitate. This precipitate was collected, washed with Et₂O (2 × 2 mL), and dried *in vacuo*.

1-Benzyl-4-[2,6-bis](dimethylamino)methyl]-1-palladium(II) bromide-benzene]-1*H***-1,2,3-triazole, 9. Brown powder, 82% yield. ¹H NMR (400 MHz, DMSO-***d***₆): δ 2.71 (s, 12H, N(CH₃)₂, 4.10 (s, 4H, CH₂N), 5.62 (s, 2H, CH₂Ph), 7.31–7.39 (m, 7H, ArH), 8.53 (s, 1H, H-triazole). ¹³C NMR (100 MHz, DMSO-***d***₆): δ 52.55, 53.87, 73.60, 117.88, 121.11, 128.20, 128.57, 128.91, 129.51, 136.58, 145.56, 146.51, 148.03. MALDI-TOF (9-nitroanthracene, MeCN) (***m***/***z***): 542.14 (calcd M – Br 454.12). Anal. Calcd for C₂₁H₂₆-ClN₅Pt·4H₂O: C, 41.56; H, 5.65; N, 11.54. Found: C, 41.80; H, 5.12; N, 11.35. IR: ν_{triazole} 1450–1430 cm⁻¹.**

1-Benzyl-4-[2,6-bis](**dimethylamino)methyl]-1-platinum**(**II**) **bromide-benzene]-1***H***-1,2,3-triazole**, **10.** Off-yellow powder, 96% yield. ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.92 (s, 12H, N(CH₃)₂, 4.07 (s, 4H, CH₂N), 5.58 (s, 2H, CH₂Ph), 7.25 (s, 2H, ArH), 7.30–7.37 (m, 5H, ArH), 8.43 (s, 1H, H-triazole). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 53.63, 55.60, 77.27, 116.89, 120.84, 126.12, 128.53, 128.80, 129.46, 138.82, 144.84, 146.70, 148.99. MALDI-TOF (9-nitroanthracene, MeCN) (*m*/*z*): 578.15 (calcd 578.15), 542.17 (calcd M – Cl 542.64). Anal. Calcd for C₂₁H₂₆ClN₅Pt: C, 43.56; H, 4.53; N, 12.10. Found: C, 43.67; H, 4.50; N, 12.06. IR (ATR): $ν_{triazole}$ 1450–1430 cm⁻¹.

Synthesis of 3-Aminopropyl-1-silica. Silica (5 g, BASF bv nederland, C500-383) and 3-aminopropyl-1-(triethoxy)silane (5 mL, 0.021 mol) were placed in dry toluene (100 mL) and heated at reflux for 24 h. The mixture was filtered hot, then washed with toluene (2×), boiling EtOH (2×), acetone (2×), CH₂Cl₂ (2×), and pentane (2×), and subsequently dried under vacuum. White powder. IR (DRIFT, difference): ν_{SiO-H} 3740 cm⁻¹ (trough).

Synthesis of TMS-capped-3-aminopropyl-1-silica. 3-Aminopropyl-1-silica (5 g) was placed in dry hexanes (50 mL) with hexamethyldisilazane (5 mL, 3.87 g, 0.024 mol), and the mixture was heated at reflux for 24 h. The mixture was filtered hot, then washed with pentane (2×), boiling EtOH (2×), CH₂Cl₂ (2×), and pentane (2×), and subsequently dried under vacuum. White powder. IR (DRIFT, difference): v_{SiO-H} 3740 cm⁻¹ (trough).

Synthesis of TMS-capped-3-isocyanatopropyl-1-silica, 2. TMScapped-3-aminopropyl-1-silica (5 g) was placed in a Schlenk with toluene (30 mL, dry degassed). Triphosgene (2.03 g, 6.8 mmol) was added, and the resulting mixture was heated at reflux for 24 h. The mixture was filtered hot, then washed with toluene (2×), acetone (2×), CH₂Cl₂ (2×), and pentane (2×), and subsequently dried under vacuum. White powder. IR (DRIFT, difference): ν_{CNO} 2276 cm⁻¹, ν_{SiO-H} 3740 cm⁻¹ (trough). Anal. Found: C 7.47, H 2.20, N, 0.77.

Synthesis of TMS-capped-3-(benzylcarbamato)propyl-1-silica, 6. TMS-capped-3-isocyanatopropyl-1-silica (1 g) was placed in dry toluene (5 mL) with benzyl alcohol (1 mL, 9.7 mmol) and stirred at reflux for 24 h. The mixture was filtered hot, then washed with toluene (2×), boiling EtOH (2×), acetone (2×), CH₂Cl₂ (2×), and pentane (2×), and subsequently dried under vacuum. White powder. IR (DRIFT, difference): $\nu_{carbamate}$ 1700 and 1530 cm⁻¹, ν_{CNO} 2276 cm⁻¹ (trough), ν_{SiO-H} 3740 cm⁻¹ (trough).

Synthesis of TMS-capped-3-[4-(*N*-carbamato)-2,6-bis](dimethylamino)methyl]-1-palladium(II) bromide-benzene]propyl-1-silica, 7. 4-(*tert*-Butyldimethylsiloxy)-2,6-bis](dimethylamino)methyl]-1-palladium(II) bromide-benzene (0.05 g, 0.11 mmol) was dissolved in a CH₂Cl₂/MeOH mixture (1:1, 10 mL) and stirred over an ion-exchange resin (DOWEX 50WX8) for 6 h (small amount of Pd black observed). The resulting solution was filtered and solvent was removed. The resulting solution was dissolved in CH₂Cl₂ (20 mL) with NEt₃ (3 mL, large excess), 4-dimethylaminopyridine (0.005 g, cat., 0.04 mmol), and TMS-capped-3-isocyanatopropyl-1-silica (1 g) and was stirred at reflux for 24 h. The mixture was filtered hot, then washed with EtOH (2×), acetone (2×), CH₂Cl₂ (2×), and pentane (2×), and subsequently dried under vacuum. Light yellow powder. IR (DRIFT, difference): $\nu_{\text{carbamate}}$ 1641 and 1562 cm⁻¹, ν_{CNO} 2276 cm⁻¹ (trough), $\nu_{\text{SiO-H}}$ 3740 cm⁻¹ (trough). Anal. Found: C 6.45, H 1.81, N, 2.12, Pd 0.26.

Synthesis of TMS-capped-3-[4-(*N*-carbamato)-2,6-bis](dimethylamino)methyl]-1-platinum(II) chloride-benzene]propyl-1-silica, 8. 4-(*tert*-Butyldimethylsiloxy)-2,6-bis[(dimethylamino)methyl]-1-platinum(II) chloride-benzene (0.054 g, 0.1 mmol) was dissolved in a CH₂Cl₂/MeOH mixture (1:1, 10 mL) and stirred over an ion-exchange resin (DOWEX 50WX8) for 24 h. The resulting solution was filtered and solvent was removed. The resulting solution was filtered and solvent was removed. The resulting solid was dissolved in CH₂Cl₂ (20 mL) with NEt₃ (3 mL, large excess), 4-dimethylaminopyridine (0.005 g, cat., 0.04 mmol), and TMS-capped-3-isocyanatopropyl-1-silica (1 g) and was stirred at reflux for 24 h. The mixture was filtered hot, then washed with EtOH (2×), acetone (2×), CH₂Cl₂ (2×), and pentane (2×), and subsequently dried under vacuum. Yellow powder. IR (DRIFT, difference): $\nu_{carbamate}$ 1648 and 1548 cm⁻¹, ν_{CNO} 2276 cm⁻¹ (trough), ν_{SiO-H} 3740 cm⁻¹ (trough). Anal. Found: C 11.62, H 2.53, N, 2.17, Pt 0.79.

Standard Conditions for Double Michael Addition. Catalyst (0.0025 mmol active cat.), cyanoacetic acid ethyl ester (0.03 g, 0.25 mmol, ethyl cyanoacetate), 3-buten-2-one (0.056 g, 0.79 mmol, methyl vinyl ketone), and diisopropylethylamine (Hünigs base, 0.005 g, 0.025 mmol) were placed in CH₂Cl₂ (1 mL, dry degassed). The mixture was stirred at room temperature until the reaction was complete. Aliquots of 10 μ L were taken at regular time intervals (varied depending on whether homo or hetero cat.). All volatiles were then removed under a steady stream of nitrogen, and the remaining oil was dissolved in CDCl₃ for ¹H NMR analysis.

Standard Conditions for Allylic Stannylation. Catalyst (0.0026 mmol active cat.), hexamethyldistannane (0.082 g, 0.25 mmol), and 3-chloro-1-propenylbenzene (0.38 g, 0.25 mmol, cinnamyl chloride) were placed in dry, degassed THF (1 mL). The mixture was stirred at room temperature until the reaction was complete. Aliquots of 10 μ L were taken at regular time intervals (varied depending on whether homo or hetero cat.). All volatiles were then removed under a steady stream of nitrogen, and the remaining oil was dissolved in CDCl₃ for ¹H NMR analysis.

Recycling. Catalytic mixtures were poured over a glass frit (#4) and subsequently washed with the solvent used during the catalytic experiment (CH₂Cl₂ for Michael, THF for both stannylation and allylic alkylation). This method led to loss of some catalytic material, which could not be removed from the frit. Another technique is to centrifuge the reaction mixture to separate the insoluble catalytic material.

Sequential Experiments: Standard Conditions for Allylic Alkylation. Catalyst (0.0026 mmol active cat., a PCP-Pd complex tethered to silica previously synthesized in our group¹⁹) and 4-nitrobenzaldehyde (0.038 g, 0.25 mmol) were placed in the dry, degassed filtrate solution from the allylic stannylation reaction. Material **4** was removed prior to addition of the PCP-Pd catalyst and nitrobenzaldehyde using the same technique used for catalyst recycling mentioned above (the stannylation reaction mixture was placed in a centrifugation vessel, and the catalyst and substrates were separated from each other, followed by filtration). The mixture was stirred at room temperature for 24 h. All volatiles were then removed under a steady stream of nitrogen, and the remaining oil was dissolved in CDCl₃ for ¹H NMR analysis.

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