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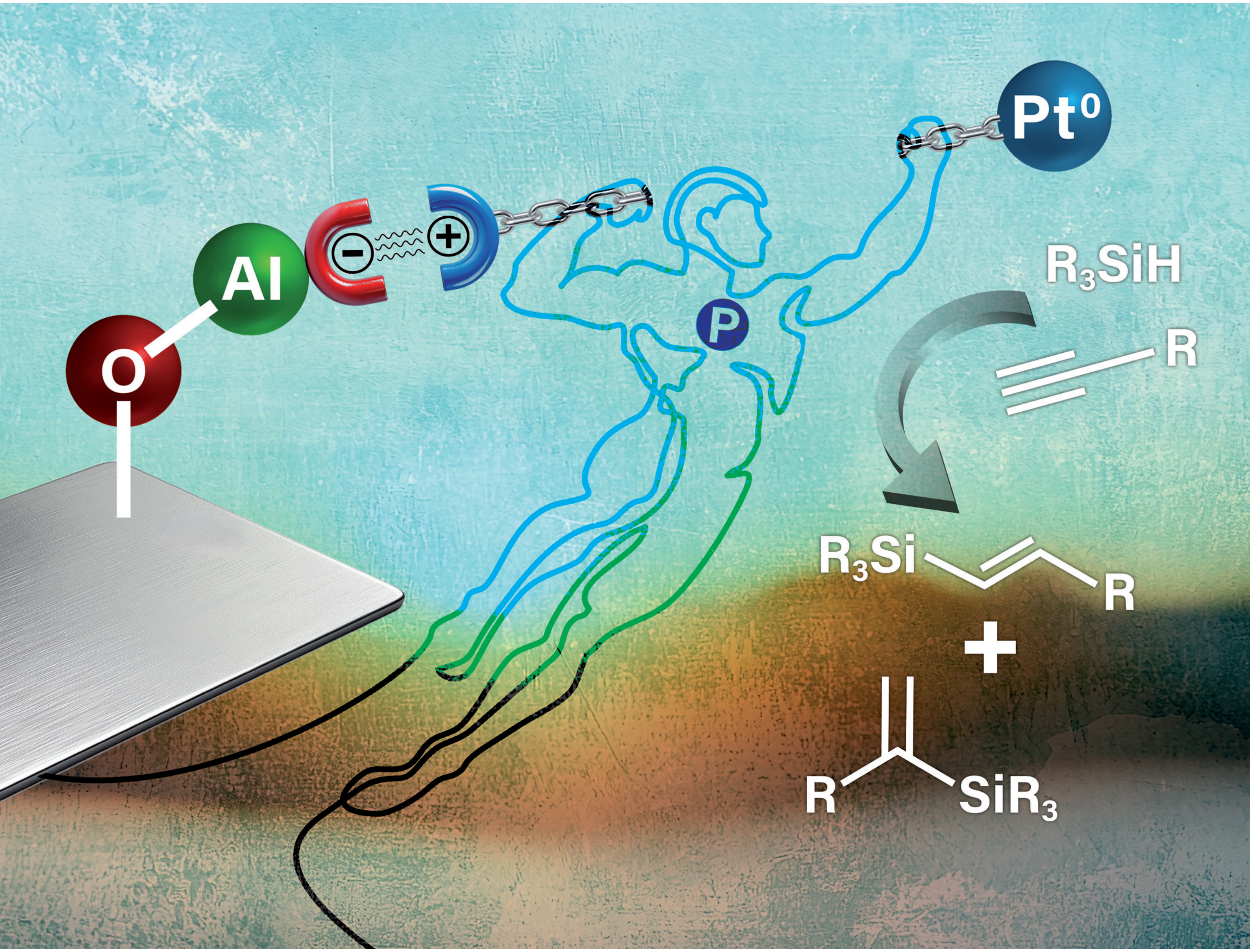

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Well-defined Pt(0) heterogeneous hydrosilylation catalysts supported by a surface bound phosphenium ligand†

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Single atom, low valent transition metals are important for heterogeneous catalysis but are challenging to generate and stabilize in a well-defined manner. Herein, we explored the functionalization of silica with well-defined N-heterocyclic phosphenium (NHP) ions to heterogenize low-valent metals. The surface electrostatically bound [NHP]$^+$ ions coordinate to Pt(0) precursors, resulting in well-defined, chemisorbed [(NHP)Pt(0)L$_n$]$^+$ sites. The resulting materials catalyze the hydrosilylation of alkynes and exhibit activities and selectivities that rival the current industry standard homogeneous catalysts. The catalysts leach Pt, limiting their recyclability; however, recycling studies support that the high regioselectivities arise from heterogeneous sites and Pt particles do not form on the surface. We suspect that this phosphenium-based immobilization strategy will result in stable, tunable, low valent heterogeneous transition metal catalysts in a wider array of catalytic reactions.

Introduction

Platinum group-containing heterogeneous catalysts are important for hydrogenation, alkane dehydrogenation, oxidation, and other reactions.[1–5] Stabilizing low-valent platinum group metals using oxide supports, however, remains a challenge. For instance, traditional nanoparticle-based catalysts are prone to sintering, which leads to a decrease in activity over time. These catalysts also show poor metal utilization, with only a small percentage of the precious metal often being catalytically active. Single atom catalysts (SACs) have shown promise in improving the homogeneity of active site structures and activity; however, they often suffer from poor stability and tunability and require low metal loadings to reduce sintering.[6–12] Surface organometallic chemistry (SOMC) is a related field[13] that utilizes molecular and solid-state techniques to anchor molecular species onto solid supports with well-defined structures.[14–20] Traditionally, the metal is chemisorbed onto the surface of an oxide *via* protonolysis, requiring reactive metal-X species (X = alkyl, amide, alkoxide), with a metal oxidation state greater than zero (Fig. 1A). Pt group metals in the +2 oxidation state have been chemisorbed onto oxide surfaces for applications such as cross-coupling,[21] hydrogenation,[22] copolymerization of acrylate monomers and ethylene,[23–25] and olefin isomerization.[26] Well-defined surface organometallic Pt(II/IV)

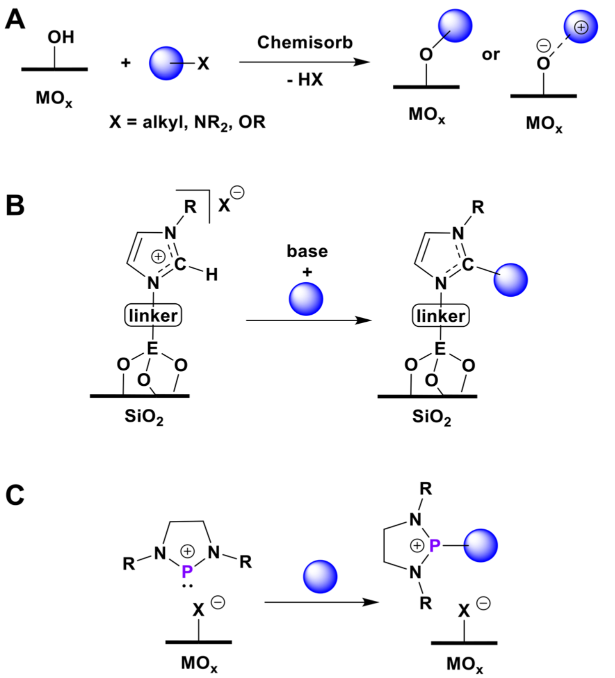

Fig. 1 (A) Traditional SOMC chemisorption reaction. (B) NHC tethered to silica for the support of a metal. (C) This work: support of metal catalysts *via* surface bound phosphenium ions.

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species, however, decompose to form low valent nanoparticles under reducing conditions for heterogeneous alkane dehydrogenation,[27] polyolefin upcycling,[28] and others.[29] To date, no reports have been disclosed regarding the stabilization of well-defined, formally Pt(0), monometallic surface species.

There is a long history of the use of dative ligands, such as N-heterocyclic carbenes (NHCs), for supporting low valent metals for catalysis in molecular systems.[30,31] In heterogeneous systems, NHCs have been applied as a tether to covalently affix metals to solid supports such as graphene, polymers, and silica (Fig. 1B).[21,32,33] The syntheses of these materials are often challenging and require many steps, adding barriers to their adoption in industrial processes. Complexity is further increased by the fact that NHCs are often unstable and require *in situ* formation with a base in the presence of the metal precursor.

N-heterocyclic phosphenium ($[NHP]^+$) ions are isolobal with NHCs and coordinate to transition metals in low oxidation states,[34–40] including Pt(0).[41–43] In this work, an $[NHP]^+$ ion was formed on the surface of an oxide and utilized as a ligand to immobilize Pt(0) complexes (Fig. 1C). The well-defined $(NHP)^+$–Pt(0) complexes were applied to heterogeneous alkyne hydrosilylation catalysis and compared to other leading catalysts, including the current industrial standard.

Results and discussion

Conley and co-workers reported that $^iPr_3Si^+$ and $Al(OC(CF_3)_3)_3$ functionalized $SiO_{2\text{-}700}$ ($[^iPr_3Si][ASO]$)[44] and a related material ($[^iPr_3Si][SZO]$) abstracted chloride ions from metal chloride salts to generate well-defined Pd(II) and Ir(I) catalysts, and chlorosilanes as by-products.[25,45] Similarly, molecular phosphenium ions have been synthesized by abstraction of halides from NHPX precursors with Me_3SiOTf and related silicon-based electrophiles.[40] We thus decided to adapt Conley's grafting strategy to generate electrostatically bound surface $[NHP]^+$ ligands. To this end, we reacted DippNHPCl (Dipp = 2,6-diisopropylphenyl) with $[^iPr_3Si][ASO]$ to produce the surface bound phosphenium ion [DippNHP][ASO] (**1**) and $^iPr_3SiCl$ (Fig. 2A).

To determine whether the phosphenium ion was indeed generated in **1** as expected, we utilized solid-state ^{31}P NMR spectroscopy. The ^{31}P NMR chemical shift is known to be sensitive to the formation of phosphenium ions.[35,36,46–48] The ^{31}P solid-state NMR (SSNMR) spectrum of **1** (Fig. 2B) contains an isotropic chemical shift at 273 ppm, which is comparable to the chemical shift of analogous $[MesNHP][Bar^F{}_4]$ (^{31}P chemical shift = 257 ppm) reported by Baker and co-workers, and distinctly different from the value of 154 ppm measured for the DippNHPCl precursor, supporting the structural assignment.[49] The ^{31}P SSNMR spectrum of **1** contains a number of spinning sidebands due to the large chemical shift anisotropy (CSA, see the ESI for details†) that results from the low coordinate P cation. In solution, $[NHP]^+$ ions are known to coordinate Pt(0); therefore, we hypothesized that **1** will support Pt(0) and effectively chemisorb Pt(0) single atoms onto the surface of silica.

1 reacts with $(Ph_3P)_2Pt(C_2H_4)$ to generate $[(DippNHP)Pt(PPh_3)_2][ASO]$ (**2**) and ethylene (Fig. 2A). The ^{31}P SSNMR spectrum (Fig. 2C and D) of **2** contains signals at 294 ($^1J_{Pt\text{–}P}$ = 6400 Hz) and 45 ($^1J_{Pt\text{–}P}$ = 4200 Hz) ppm, assigned to the $[DippNHP]^+$ and PPh_3 ligands bound to Pt, respectively. The ^{31}P chemical shifts and $^1J_{Pt\text{–}P}$ couplings are similar to the molecular analogue $[(MesNHP)Pt(PPh_3)_2][OTf]$ (^{31}P chemical shift = 289.0 ($^1J_{Pt\text{–}P}$ = 6498 Hz) and 43.9 ($^1J_{Pt\text{–}P}$ = 4237 Hz) ppm), supporting the structural assignment.[41] **1** also reacts with Karstedt's catalyst ($Pt(dvtms)_n$, dvtms = 1,3-divinyltetramethyldisiloxane) to produce [(DippNHP)Pt(dvtms)][ASO] (**3**) (Fig. 2E), which is analogous to the highly active and selective (NHC)Pt(dvtms) hydrosilylation catalysts reported by Markó and co-workers.[30,50] The ^{31}P SSNMR spectrum of **3** exhibits overlapping signals of unreacted $[DippNHP]^+$ and $[(DippNHP)Pt(dvtms)]^+$ at 277 ppm, close to the value of 272 ppm measured for a triflate analogue (see the ESI†). All attempts at acquiring ^{195}Pt NMR spectra either directly or *via* indirect detection through ^{31}P,[51] were unsuccessful due to short relaxation times. Accordingly, even attempts at performing ^{31}P CPMAS NMR were also unsuccessful. Pt and P ICP-OES measurements of **3** indicate that 84% of the $[DippNHP]^+$ ligands react with Pt, supporting the presence of unreacted $[DippNHP]^+$ (see Table S3 for details†). Solution NMR analyses of the reaction of **2** with PMe_3 and **3** with PPh_3 resulted in the desorption of 1.9 (±2) equivalents of PPh_3 and 1.07 (±7) equivalents of dvtms per Pt, respectively, further supporting the assigned Pt coordination environments for **2** and **3** as $(dippNHP)Pt(PPh_3)_2$ and (dippNHP)Pt(dvtms), respectively.

One of the most important applications of low valent Pt is catalytic hydrosilylation of olefins and alkynes.[52–56] Pt catalyzed hydrosilylation is challenging to perform with heterogeneous catalysts due to poor reactivities, selectivities, and metal leaching into the solution.[53,55,57–59] There are limited examples of well-defined heterogeneous Pt,[60–63] Rh,[64–66] and other[67] hydrosilylation catalysts generated using SOMC techniques; moreover, most reported systems have poor activity, selectivity, or stability.

Catalysts **2** and **3** were subjected to standard 1-octyne hydrosilylation conditions (Table 1)[30,52–55] and compared to homogeneous catalysts for activity and product regioselectivity.[68] Catalyst **2** is modestly active but highly regioselective for the β-(*E*) isomer (β-(*E*) : α = 11) at 0.4 mol% loading of Pt when compared to Markó and co-workers' (IPr)Pt(dvtms) (Pt = 0.005%, 22 h, β-(*E*) : α = 11.5) catalyst[69] and the $(PPh_3)_2Pt(C_2H_4)$ precursor (β-(*E*) : α = 4.8, see the ESI†), while selectivity and reactivity are considerably reduced at a lower Pt loading of 0.04%. The modest catalytic activity of **2** is likely due to the inhibition of the catalyst by PPh_3.

Catalyst **3** exhibits comparable activities and selectivities to (NHC)Pt catalysts in solution.[30,69–71] This makes **3** more active than most other heterogeneous alkyne and alkene hydrosilylation catalysts synthesized using SOMC techniques[62,64–66,72] or nanoparticles[73,74] under similar conditions. The regioselectivity of **3** is nevertheless lower than that reported for analogous (IPr)Pt(dvtms), suggesting that the regioselectivity may not be entirely controlled by the steric bulk of the NHP ligand,

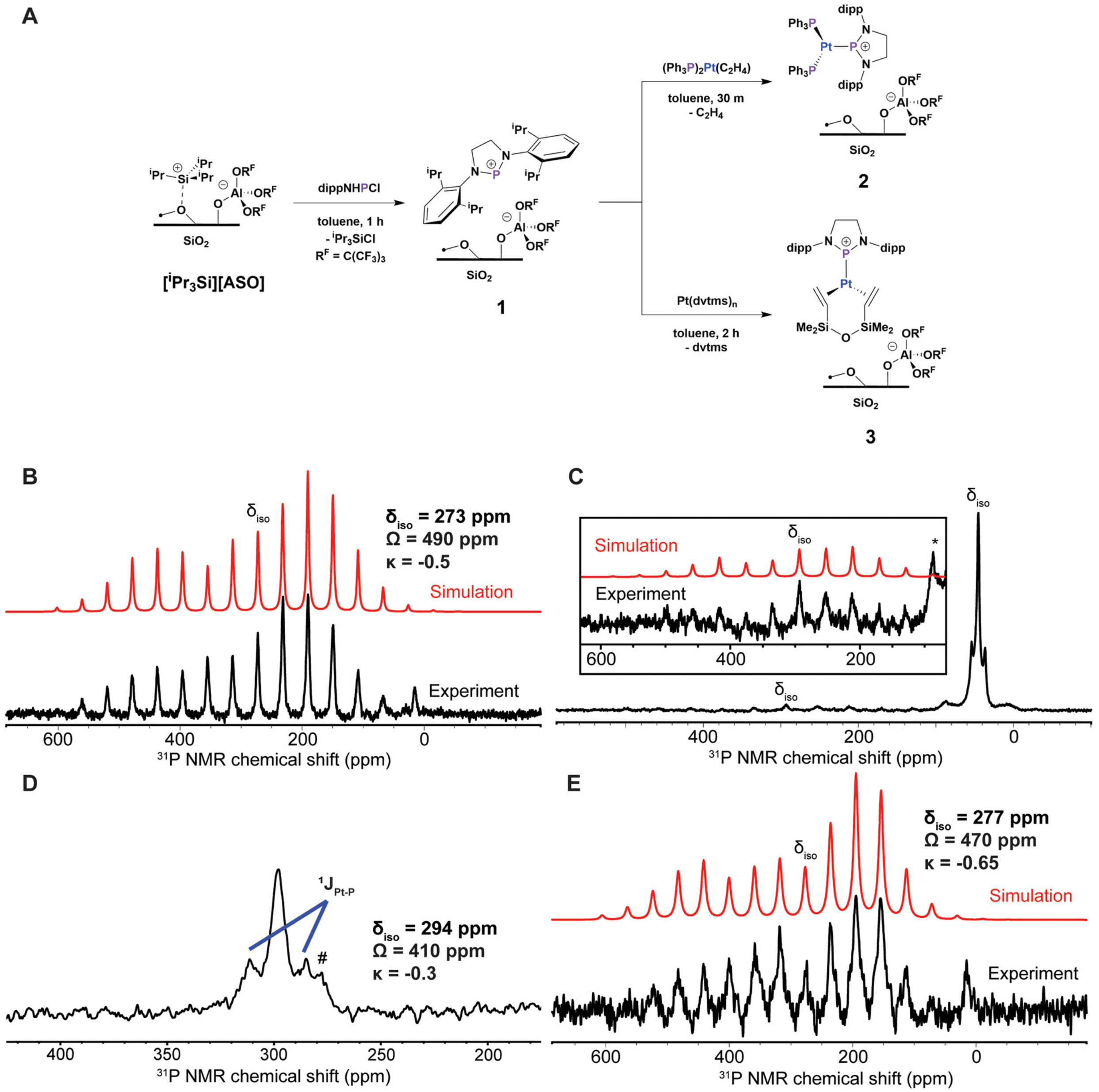


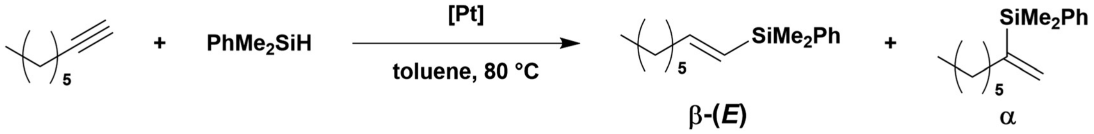
Fig. 2 (A) Scheme for the synthesis of **1**, **2**, and **3**. Experimental ^{31}P SSNMR spectra (black) and simulations (red) of **1** (B), **2** (C and D), and **3** (E). The inset in (C) shows an expansion of the $[(\mathrm{DippNHP})\mathrm{Pt}]^+$ signal. δ_{iso} = isotropic chemical shift. The spectra in (B), (C), and (E) were acquired while spinning at 10 kHz. D is the $[(\mathrm{DippNHP})\mathrm{Pt}]^+$ signal in the ^{31}P SSNMR spinning at 30 kHz and # denotes a small quantity of unreacted **1**.

as was reported in the case of NHCs. Further studies are being conducted to determine the root cause for the reduced selectivity.

DippNHPCl reacts with ~50% of the $[^i\mathrm{Pr_3Si}][\mathrm{ASO}]$ sites (based on Al loading)[44] in the synthesis of **1**; therefore, it is feasible that the unreacted $[^i\mathrm{Pr_3Si}]^+$ reacts with Pt(0) to form Pt → Si Lewis pairs or formally oxidize the Pt(0) to $[\mathrm{Pt(II)(Si(iPr)_3)}]^+$ sites that may catalyze the hydrosilylation reaction. To assess these possibilities, $(\mathrm{Ph_3P})_2\mathrm{Pt}(\mathrm{C_2H_4})$ and Karstedt's catalyst were absorbed onto $[^i\mathrm{Pr_3Si}][\mathrm{ASO}]$ (without the $[\mathrm{NHP}]^+$ ligand) utilizing the same conditions for the synthesis of **2** and **3**, yielding **4** and **5**, respectively. SSNMR and ICP analyses indicate that both precursors absorb onto the surface, albeit in ~5× lower concentrations than **2** and **3**. **4** and **5** both catalyze the hydrosilylation of 1-octyne with dimethylphenylsilane under similar conditions to **2** and **3** with slightly lower product yields, which may be attributed to the reduced Pt loadings; however, both catalysts produce silanes with lower regioselectivities that are comparable to the molecular precursors, indicating that the surface species are most likely physisorbed precursor molecules that desorb during catalysis.

A significant benefit of stable heterogeneous catalysts is their recyclability. Owing to the chemisorption of Pt in **2** and **3**, we hypothesized that they will be more recyclable than **4**

Table 1 Summary of the 1-octyne hydrosilylation catalysis results[a]



Material	Pt loading (mol %)	Time[b] (h)	1-octyne conv. (%)	$PhMe_2SiH$ conv. (%)	Combined yield[c] (%)	Product TON[c]	Product TOF[c]	β-(*E*) : α[c,d]
2	0.43 (4)	20	>99.9	90.4 (6)	88 (1)	205 (2)	10	11 (1)
2	0.043 (4)	48	23 (1)	21 (2)	22 (3)	510 (60)	11	6.6 (2)
3	0.058 (2)	0.17	>99.9	91.5 (2)	84 (1)	1460 (10)	8600	6.96 (4)
3	0.0058 (2)	2	97 (3)	99.5 (5)	86 (2)	14 900 (300)	7450	6.20 (3)
4	0.12 (1)[e]	20	>99.9	89.2 (1)	80 (1)	646 (5)	32	4.6 (2)
5	0.011 (2)[f]	0.5	94.3 (1)	98.3 (2)	85.3 (4)	7920 (40)	15 840	5.30 (1)

[a] Typical catalysis conditions: catalyst + 0.5 M 1-octyne/$PhMe_2SiH$ in toluene at 80 °C (see the ESI for more details†). Average of 2 runs. Errors are provided in parentheses. [b] Time to achieve the indicated conversions of 1-octyne or $PhMe_2SiH$. [c] Combined yield, TON (mol products mol Pt^{-1}), and TOF (mol products mol Pt^{-1} h^{-1}) of the β-(*E*) and *α*-hydrosilylation products as determined by GC-FID with an internal standard of cyclooctane. The TOF was determined at the time indicated in the table and should be considered a minimum. [d] Ratio of the β-(*E*) : *α* product isomers. [e] Same relative mass of the catalyst utilized for **2** at 0.43% Pt. [f] Same mass of the catalyst used for **3** at 0.058% Pt. NR = no reaction and NA = not applicable.

and **5**. To verify this, we subjected catalysts **2**, **3**, **4** and **5** to recycling experiments. These experiments involved recovering the solid catalyst after the reaction reached partial conversion (∼40–70%). The catalysts were recovered by simple filtration, washed with toluene and used in additional reactions with fresh substrates. A summary of normalized recycling data is provided in Fig. 3 (see the ESI for full details†).

2 (0.58% Pt) was run for 2 hours and showed a steady loss in activity over 5 reactions, with an initial drop of 40% of the initial activity. **3** (0.058% Pt) showed better recyclability than **2** with only a 16% drop in the first recycling of the catalyst; however, the activity of **3** further declined for subsequent recycling attempts. Although the activities of **2** and **3** decrease with recycling, the regioselectivities remain similar throughout the 5 runs and the catalysts do not turn dark in color, supporting that the major active site is the heterogeneous [(DippNHP)Pt]$^+$ species and that particles do not form during the reaction.

Utilizing **4** and **5**, we observed initial drops in activity of 38 and 60%, respectively, after the first recycling of the catalysts. Subsequent recycling of **4** only resulted in a slow decline in activity of approximately 5%, suggesting that a stable or rebounding surface Pt species may form. In contrast to this, the activity of **5** declined by ∼50% after each recycling step, making it the poorest recycling catalyst in the study. Pt leaching may lead to active homogeneous catalyst species that may contribute to the catalytic activities and attribute to the poor recyclability. Indeed, hot filtrations of the catalytic reactions revealed that active species do form in solution (see the ESI for details†). The leaching was highest for **2** and **4**. In **3** and **5**, the reductions in activity slowed in subsequent recycling steps,

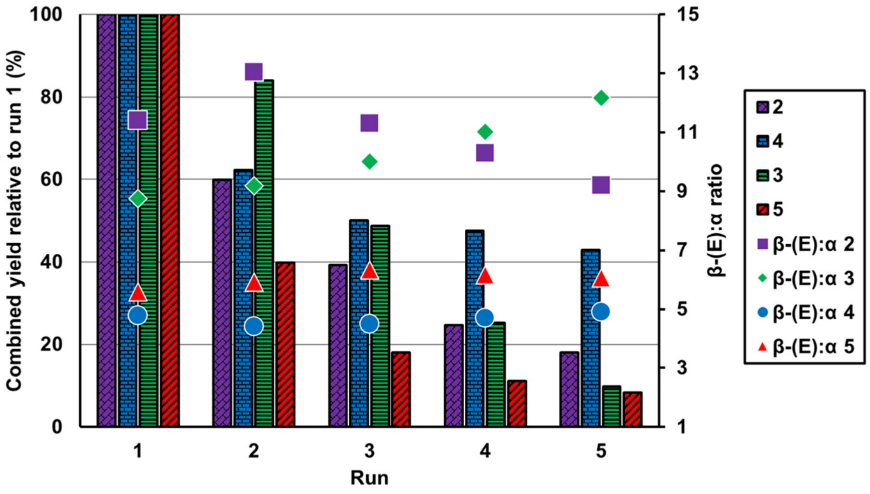


Fig. 3 Normalized recyclability of the catalysts in this study. The bars represent the relative yield of the combined β-(*E*) and *α*-hydrosilylation products compared to the initial run (run 1). The scatter plot indicates the β-(*E*) : *α* isomer ratio in each run.

suggesting a reduction in Pt leaching. The limited recyclability and hot filtration study of **3** suggest that the catalyst is primarily heterogeneous.

Conclusions

In summary, silica was functionalized with well-defined phosphenium ions. The phosphenium ions coordinate to Pt(0), resulting in chemisorbed Pt(0) sites with well-defined structures analogous to molecular complexes. The chemisorbed Pt (0) sites heterogeneously catalyze the hydrosilylation of alkynes with activities and selectivities comparable to those of molecular catalysts. Stable solid catalysts can be further recycled and reused for a number of independent reactions due to their heterogeneous nature. Further investigation utilizing similar strategies from this study is underway and anticipated to discover more stable catalysts for hydrosilylation and other catalytic reactions.

Author contributions

All authors contributed to the project design. D. B. C. performed the laboratory syntheses and material characterization studies. D. B. C. and M. M. performed the SSNMR experiments under the direction of F. A. P. M.-C. K. performed the electron microscopy experiments under the direction of L. Z. The manuscript was written through contributions by all authors. All authors have given approval to the final version of this manuscript.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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