Hybrid Materials for Single-Atom Catalysis

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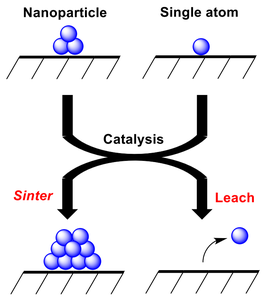
Challenges in the isolation of zero-valent single-atoms for catalysis

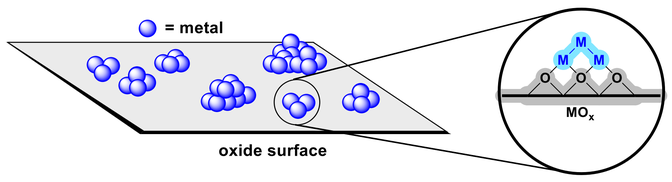


Stability

Low valent particles/atoms absorbed to supports are often active catalysts for a variety of chemical transformations. However, non-covalent metal-support interactions are relatively weak resulting in agglomeration or leaching under reducing catalysis conditions, leading to a loss in activity and selectivity.

Control over structure

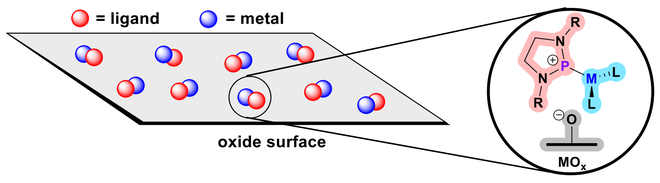
The structure of adsorbed particles/atoms and metal–support bonding is difficult to control, limiting atomic-level structural precision in heterogeneous catalysts. As a result, establishing structure–activity relationships (SAR) is extremely challenging, and catalyst improvements often rely on trial-and-error rather than rational, structure-guided design.



Which begs the question:

How do we stabilize single atom M^0 surface catalysts and incorporate SAR?

Phosphenium ligands: Simple to prepare, modular, & powerful tools for study

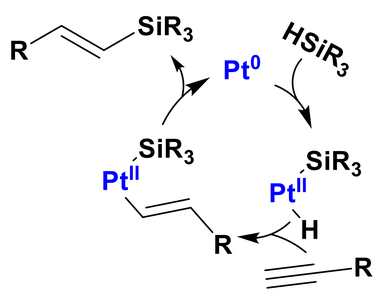


Advantages:

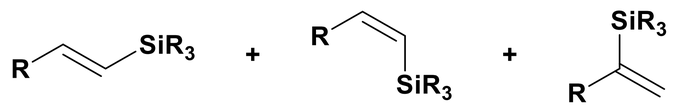
- Simple to synthesize from affordable and scalable precursors
- Many are stable and isolable with diverse steric and electronic structures
- Controllable structures give isolated metal atoms
- ^{31}P NMR spectroscopy is sensitive to structure and electronic changes.

Case Study: Highly active and regioselective catalytic alkyne hydrosilylation

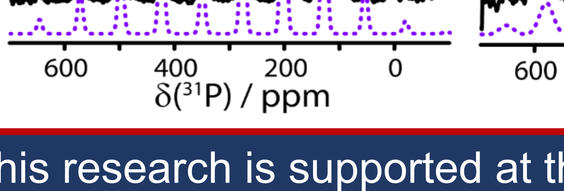
Heterogeneous hydrosilylation of olefins and alkynes is challenging because Pt(0) catalysts are unstable, leading to poor recyclability, activity, and selectivity. Their particle-based nature also limits steric control, resulting in low regioselectivity. In contrast, homogeneous catalysts use ligands to tune structure–activity relationships. Since Pt(0) plays a key role in hydrosilylation, this reaction serves as an ideal testbed for evaluating new heterogeneous catalyst designs.



Possible products:
We only want one!



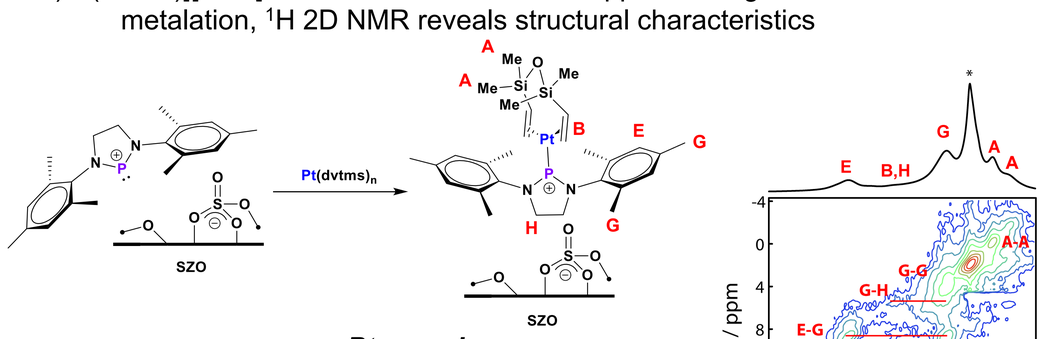
Precatalyst synthesis and characterization[1,2]



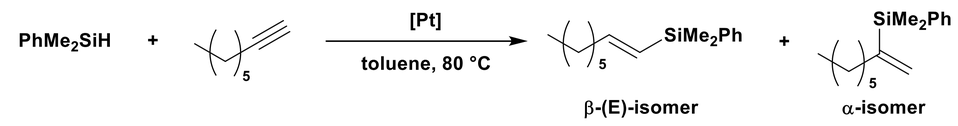
Silylated strongly-acidic oxides react with NHPCl to form well-defined surface-bound phosphenium ligands that coordinate Pt(0) precursors.

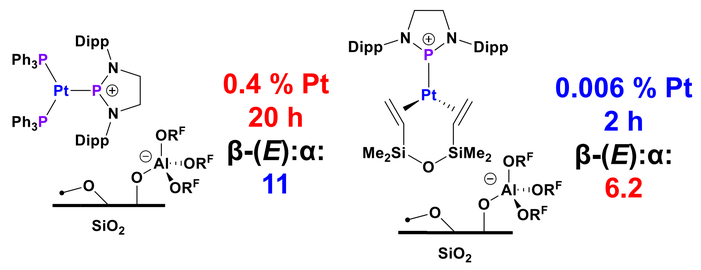
Solid-state NMR is central to characterizing these new precatalysts. Examples:

- [MesNHP][SZO] NMR: Confirms P^+ formation – high chemical shift and large CSA
- [(MesNHP)Pt(dvtms)][SZO] NMR: ^{31}P chemical shift supports charge remains on P after metalation, ^{1}H 2D NMR reveals structural characteristics



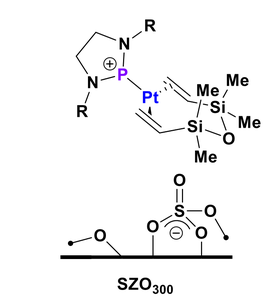
Ligand & surface control over catalysis regioselectivity



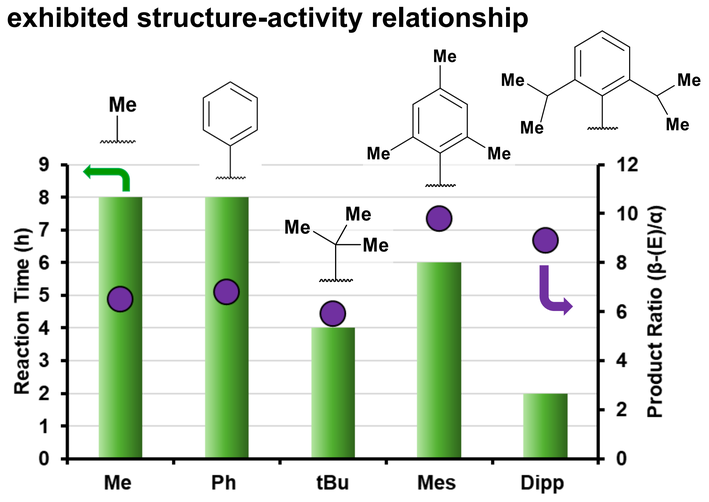


The first generation $(NHP)^+$-Pt(0) catalysts catalyze the hydrosilylation reaction with *comparable regioselectivity* ***or*** *activities* to the best molecular catalysts.[1]

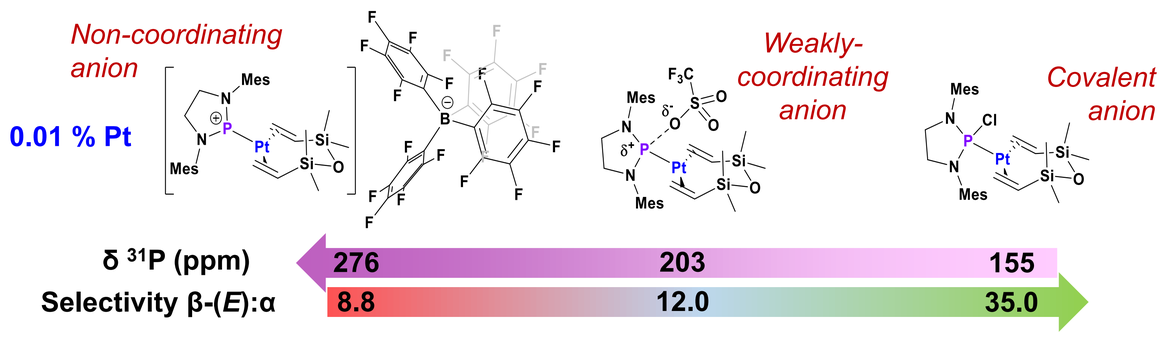
Next generation: Sulfated zirconia exhibited structure-activity relationship control and higher selectivity[2]



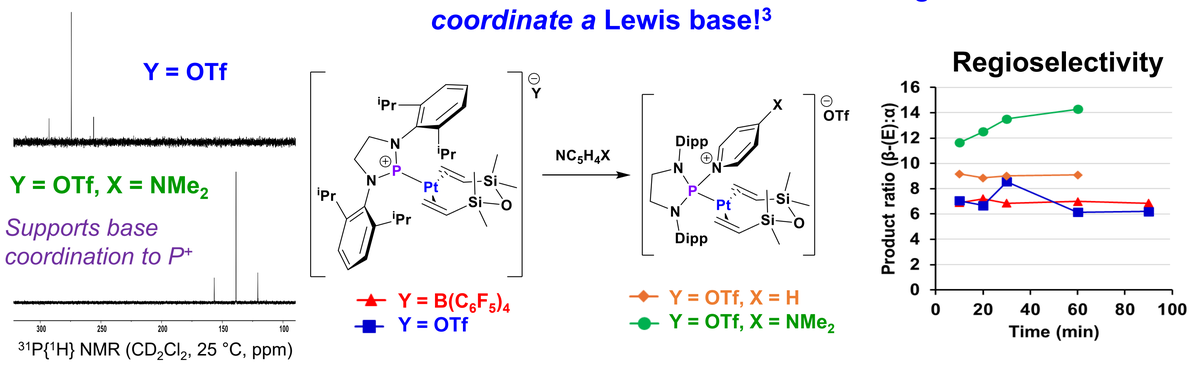
Why is SZO superior to silica?



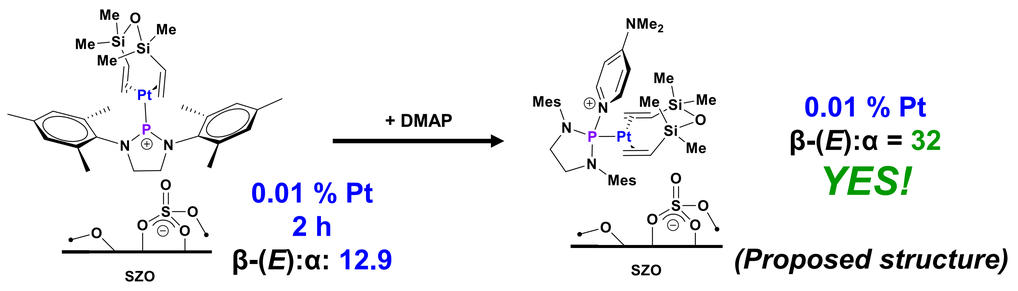
Does the anion effect catalysis and structure?



How do we emulate the covalent anion effect? The *P^+ is a strong Lewis acid so coordinate a* Lewis base![3]



Does the effect translate back to the heterogeneous system?



0.01 % Pt
2 h
β-(E):α: 12.9

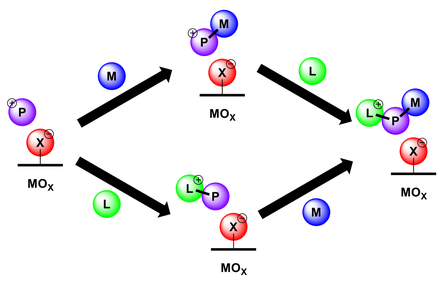
0.01 % Pt
β-(E):α = 32
YES!

(Proposed structure)

These results are the 1st step towards the design of new heterogenous catalysts that are more stable, reactive, efficient, and selective for a variety of metals and important chemical processes.

The next generation: modular ligands for highly active, stable, and selective catalysts

Taking advantage of the Lewis acidic ligands, we can further adjust the structure and electronics to control the activity and selectivity of hydrosilylation and other reactions.



References and other acknowledgements

References: 1.) Culver, D. B.; Mais, M.; Kang, M. C.; Zhou, L.; Perras, F. A. *Dalton Trans.* **2025**, *54* (21), 8392–8399. **2.**) Culver, D. B.; Neill, C.; Perras, F. A.; Halder, M.; Chartouni, A. *Inorg. Chem.* **2026**, 65(8), 4344-4350. 3.) Kaumini, M. G.; Mais, D.; Nelson, E; Downing, A.; Perras, F. A.; Basemann, K.; Culver, D. B. *Manuscript in preparation*.

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Title: Hybrid Materials for Low-Valent Single-Atom Catalysis

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Abstract: Developing heterogeneous catalysts with molecularly well-defined active sites remains a longstanding challenge because conventional materials typically suffer from broad structural distributions and inefficient metal utilization. To address this limitation, we are developing a modular strategy based on new organic–inorganic hybrid materials (OIHMs) designed to stabilize low-valent, single-atom transition metal centers on oxide supports. Functionalizing acidic oxide surfaces with surface-generated phosphorus cations yields strong, isolating donor ligands through a streamlined, low-waste synthetic route. This framework enables access to formally zero-valent metal sites with precise molecular control over the local coordination structure. Using platinum as a representative example, this platform generates atomically dispersed, ligand-controlled fully reduced platinum active sites that exhibit high activity and regioselectivity for alkyne hydrosilylation. Catalytic performance matches or exceeds benchmark homogeneous systems while preserving the operational advantages of a solid catalyst. Crucially, the OIHM architecture allows systematic variation of both ligand identity and support composition, enabling precise structure–activity relationship studies that directly link local coordination environments to catalytic performance. Spectroscopic analyses, including solid-state NMR and infrared spectroscopy, confirm the uniform nature of the supported metal centers and provide structural insight into surface metal–ligand bonding. Harnessing the Lewis acidity of the phosphorus cations, we are currently developing asymmetric ligand environments to further enhance activity, selectivity, and stability across a broader range of metals and transformations. Together, these results establish tailored hybrid supports as a general platform for stabilizing reactive low-valent metal centers, effectively bridging the gap between molecular and heterogeneous catalysis for critical material-efficient chemical transformations.