

**Iron Catalysts for Selective Anti-Markovnikov Alkene Hydrosilylation Using Tertiary Silanes**

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the critical point, the density shows a strong variation, whereas the pressure, the integral of the density over  $\mu$  at constant  $T$ , is naturally less sensitive to the superfluid transition.

In conclusion, we have performed thermodynamic measurements of the unitary Fermi gas across the superfluid phase transition at the level of uncertainty of a few percent, without any fits or input from theory, enabling validation of theories for strongly interacting matter. Similar unbiased methods can be applied to other systems, for example, two-dimensional Bose and Fermi gases or fermions in optical lattices.

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#### Supporting Online Material

[www.sciencemag.org/cgi/content/full/science.1214987/DC1](http://www.sciencemag.org/cgi/content/full/science.1214987/DC1)  
Materials and Methods  
Figs. S1 to S4  
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# Iron Catalysts for Selective Anti-Markovnikov Alkene Hydrosilylation Using Tertiary Silanes

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Alkene hydrosilylation, the addition of a silicon hydride (Si-H) across a carbon-carbon double bond, is one of the largest-scale industrial applications of homogeneous catalysis and is used in the commercial production of numerous consumer goods. For decades, precious metals, principally compounds of platinum and rhodium, have been used as catalysts for this reaction class. Despite their widespread application, limitations such as high and volatile catalyst costs and competing side reactions have persisted. Here, we report that well-characterized molecular iron coordination compounds promote the selective anti-Markovnikov addition of sterically hindered, tertiary silanes to alkenes under mild conditions. These Earth-abundant base-metal catalysts, coordinated by optimized bis(imino)pyridine ligands, show promise for industrial application.

**M**etal-catalyzed olefin hydrosilylation, which forms alkylsilanes by cleaving a silicon-hydrogen bond and adding the fragments across a carbon-carbon double bond (1, 2), finds widespread application in the commercial manufacture of silicone-based surfactants, fluids, molding products, release coatings, and pressure-sensitive adhesives (3, 4). Consequently, hydrosilylation has emerged as one of the largest-scale applications of homogeneous catalysis (5–9).

For more than three decades, precious metal compounds with Pt, Pd, Ru, and Rh have been used almost exclusively as catalysts. Platinum compounds such as Karstedt's and Speier's catalysts, Pt<sub>2</sub>{[(CH<sub>2</sub>=CH)SiMe<sub>2</sub>]<sub>2</sub>O}<sub>3</sub> (Me, methyl) and H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O/PrOH (Pr, isopropyl), respectively, are the most widely used industrial catalysts (1, 10–12), though they suffer from chemical limitations such as intolerance to amino-substituted olefins and a tendency to catalyze competing isom-

erization of the terminal alkenes to internal isomers. Undesired isomerization often necessitates subsequent purification steps that are both energy and cost intensive. Furthermore, decomposition of the catalyst to colloidal platinum contributes to unwanted side reactions and also causes discoloration of the final products.

It has been estimated that the worldwide silicone industry consumed ~180,000 troy ounces (5.6 metric tons) of platinum in 2007 and most is not recovered (13). The high cost, coupled with the increasing demands on precious metals due to fuel-cell and other emerging technologies, has increased the volatility of the platinum market (14). The combination of chemical, economic, and political challenges inspires the exploration of inexpensive and Earth-abundant catalysts using iron, manganese, and cobalt (15). At the core of this challenge is suppressing tendencies of first-row transition metals toward one-electron redox processes in favor of the two-electron chemistry associated with the heavier metals that probably make up the fundamental steps in a catalytic cycle for alkene hydrosilylation.

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In addition to cost and environmental advantages, base-metal compounds also offer the prospect of mechanistic distinctions that may overcome some of the deleterious side reactions observed for existing commercial precious metal-catalyzed processes (16, 17). Although many successful iron-catalyzed carbonyl hydrosilylations for the synthesis of alcohols have been realized (18–23), catalysts that promote industrially practiced Si-H additions to alkenes are rare. Early studies focused on iron carbonyl compounds such as  $\text{Fe}(\text{CO})_5$  and  $\text{Fe}_3(\text{CO})_{12}$  as pre-catalysts but these required either high temperatures or ultraviolet light to access the active species (24, 25). In addition to the inconvenient reaction conditions, measurable quantities of side products arising from hydrogenation, alkene isomerization, and dehydrogenative silane coupling accompany the desired Si-H addition process, limiting the utility of this class of catalyst (26).

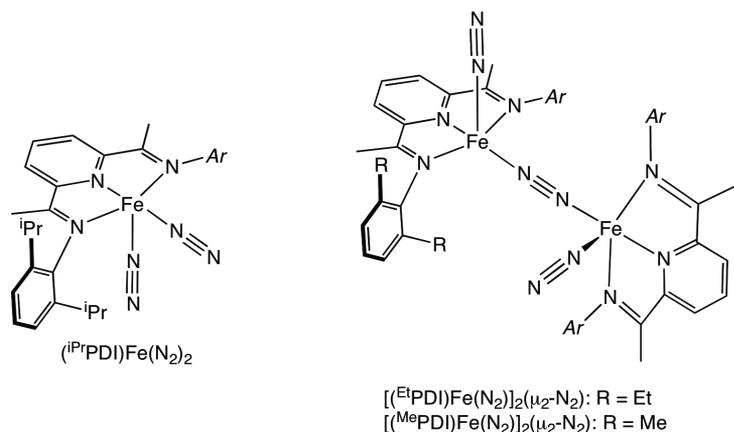
In 2004, the bis(imino)pyridine iron dinitrogen compound,  $(i^{\text{Pr}}\text{PDI})\text{Fe}(\text{N}_2)_2$  [ $i^{\text{Pr}}\text{PDI} = 2,6-(2,6\text{-}i^{\text{Pr}}_2\text{-C}_6\text{H}_3\text{N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}$ ] (Fig. 1), was reported as an effective precatalyst for the hydrosilylation of unactivated alkenes and alkynes under mild thermal conditions (27). Exclusive anti-Markovnikov addition was observed in reactions of  $\alpha$ -olefins such as 1-hexene and styrene, with no evidence for side reactions such as dehydrogenative silylation. Despite this favorable selectivity, this catalyst was unreactive toward the tertiary silane,  $\text{Et}_3\text{SiH}$  (Et, ethyl), and unactivated terminal alkenes, representing a barrier to industrial applicability. Tertiary silanes,  $\text{R}_3\text{SiH}$  (R = alkyl, aryl, alkoxide, etc.), are the most commercially relevant silicon hydrides, as products prepared from primary ( $\text{RSiH}_3$ ) or secondary ( $\text{R}_2\text{SiH}_2$ ) silanes contain residual Si-H bonds, which act as catalyst poisons and decrease the stability and, hence, the utility of the final product. One example of an iron-catalyzed 1,4-addition of a tertiary silane,  $(\text{EtO})_3\text{SiH}$ , to dienes has been reported by Wu *et al.* (28), although the substrate scope and application to commercially relevant alkene substrates have not been disclosed. Here, we describe iron compounds for the catalytic hydrosilylation of industrially applicable alkenes using tertiary silanes. Inspiration for these studies was derived, in part, from dramatically improved alkene hydrogenation activity observed with  $[(^{\text{Et}}\text{PDI})\text{Fe}(\text{N}_2)]_2(\mu\text{-N}_2)$  and  $[(^{\text{Me}}\text{PDI})\text{Fe}(\text{N}_2)]_2(\mu\text{-N}_2)$  ( $\mu$  denotes bridging ligand) (29). We were curious if reducing the size of the 2,6-aryl substituents from isopropyl to ethyl and methyl would have a similar effect in catalytic alkene hydrosilylation chemistry. In many examples, the new base-metal catalysts offer advantages in both activity and selectivity over currently employed precious compounds.

Our studies commenced with the hydrosilylation of 1-octene as a representative substrate. The product of the anti-Markovnikov addition of  $(\text{Me}_3\text{SiO})_2\text{MeSiH}$  (MD'M) to 1-octene is 3-octyl-1,1,1,3,5,5,5-heptamethyltrisiloxane (Table 1), which is prepared commercially for use as an agricultural adjuvant and as a sensory and

performance enhancer in cosmetic formulations (3). With 2000 parts per million (ppm) of  $(i^{\text{Pr}}\text{PDI})\text{Fe}(\text{N}_2)_2$  in the presence of neat 1-octene and MD'M, we observed more than 98% conversion to the anti-Markovnikov product (Table 1). Likewise, we also observed nearly complete conversion when  $(\text{EtO})_3\text{SiH}$  was used as the silane. In both cases, there was no evidence for any other products. Alkene hydrosilylations with  $(\text{EtO})_3\text{SiH}$  are of interest because the alkylsilane products find application as filler treatments (7). Consistent with the observations made previous-

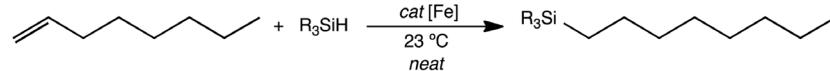
ly in toluene solution with 1-hexene (27), we observed negligible turnover with  $\text{Et}_3\text{SiH}$ . We performed each of these reactions, as well as all others reported in this study, under a dinitrogen atmosphere with predried reagents. Although this may appear to be a limitation, many large-scale, commercial reactions are performed in an inert atmosphere for safe practice.

To improve catalytic activity, we evaluated bis(imino)pyridine iron complexes with smaller aryl substituents for the catalytic hydrosilylation of 1-octene. The 2,6-diethyl-substituted compound,



**Fig. 1.** Bis(imino)pyridine iron dinitrogen complexes used for alkene hydrosilylation. Ar, aryl group.

**Table 1.** Evaluation of iron precatalysts for the selective hydrosilylation of 1-octene with various tertiary silanes. MD'M,  $(\text{Me}_3\text{SiO})_2\text{MeSiH}$ ;  $^{\text{Et}}\text{PDI}$ ,  $2,6-(2,6\text{-Et}_2\text{-C}_6\text{H}_3\text{N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}$ ;  $^{\text{Me}}\text{PDI}$ ,  $2,6-(2,6\text{-Me}_2\text{-C}_6\text{H}_3\text{N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}$ .



Compound	ppm	mol %	Silane	Time (min)	Yield (GC-FID)
	= mg complex / kg reaction mixture	= (mol complex / mol reaction mixture) x 100			
$(i^{\text{Pr}}\text{PDI})\text{Fe}(\text{N}_2)_2$	2000*	0.05	MD'M	15	>98%
$(i^{\text{Pr}}\text{PDI})\text{Fe}(\text{N}_2)_2$	2000	0.04	$(\text{EtO})_3\text{SiH}$	15	96%
$(i^{\text{Pr}}\text{PDI})\text{Fe}(\text{N}_2)_2$	2000	0.03	$\text{Et}_3\text{SiH}$	60	trace
$[(^{\text{Et}}\text{PDI})\text{Fe}(\text{N}_2)]_2(\mu\text{-N}_2)$	2000†	0.03	MD'M	15	>98%
$[(^{\text{Et}}\text{PDI})\text{Fe}(\text{N}_2)]_2(\mu\text{-N}_2)$	2000	0.02	$(\text{EtO})_3\text{SiH}$	15	97%
$[(^{\text{Et}}\text{PDI})\text{Fe}(\text{N}_2)]_2(\mu\text{-N}_2)$	2000	0.02	$\text{Et}_3\text{SiH}$	15	9%
$[(^{\text{Me}}\text{PDI})\text{Fe}(\text{N}_2)]_2(\mu\text{-N}_2)$	200‡	0.004	MD'M	15	>98%
$[(^{\text{Me}}\text{PDI})\text{Fe}(\text{N}_2)]_2(\mu\text{-N}_2)$	500§	0.007	$(\text{EtO})_3\text{SiH}$	15	97%
$[(^{\text{Me}}\text{PDI})\text{Fe}(\text{N}_2)]_2(\mu\text{-N}_2)$	2000	0.02	$\text{Et}_3\text{SiH}$	45	>98%

Fe metal concentration: \*200 ppm; †200 ppm; ‡20 ppm; §60 ppm; ||200 ppm.

$[(^i\text{PrPDI})\text{Fe}(\text{N}_2)_2](\mu_2\text{-N}_2)$ , exhibited minimal activity for hydrosilylation with  $\text{Et}_3\text{SiH}$ , but fast and selective reactions were observed with  $(\text{EtO})_3\text{SiH}$  and MD'M (Table 1). Motivations for studying hydrosilylations with  $\text{Et}_3\text{SiH}$  include determining tertiary silane scope as well as potential industrial applications. Further reduction in size of the 2,6-aryl substituents to methyl groups produced the most active hydrosilylation catalysts for 1-octene. Unlike the  $^i\text{Pr}$  and  $\text{Et}$  variants, 2000 ppm of  $[(^{\text{Me}}\text{PDI})\text{Fe}(\text{N}_2)_2](\mu_2\text{-N}_2)$  (29) resulted in complete conversion of  $\text{Et}_3\text{SiH}$  and the olefin to the anti-Markovnikov product in 45 min at  $23^\circ\text{C}$  (Table 1). Monitoring the reaction by gas chromatography as a function of time under these conditions established 60% conversion in 15 min and 88% conversion in 30 min. Successful hydrosilylation was also achieved with 500 ppm of  $[(^{\text{Me}}\text{PDI})\text{Fe}(\text{N}_2)_2](\mu_2\text{-N}_2)$ , plateauing at 71% conversion in 2 hours. In all cases, exclusive formation of the anti-Markovnikov product of 1-octene hydrosilylation was detected by gas chro-

matography and nuclear magnetic resonance (NMR) spectroscopy.

The methyl-substituted compound also exhibited high activity and selectivity for the hydrosilylation of 1-octene with  $(\text{EtO})_3\text{SiH}$  and MD'M (Table 1). To put the results with the bis(imino)pyridine iron dinitrogen complexes in context, the hydrosilylation of 1-octene with MD'M in the presence of 30 ppm of Karstedt's catalyst proceeds to 80% conversion at  $72^\circ\text{C}$  with a detectable quantity (up to 20%) of by-products arising from alkene hydrogenation, isomerization, and dehydrogenation (10). Suppression of these unwanted side reactions has been achieved by using *N*-heterocyclic carbene-supported platinum catalysts (10).

The absence of competing olefin isomerization during the hydrosilylation of 1-alkenes and preference for anti-Markovnikov products with the bis(imino)pyridine iron dinitrogen compounds inspired additional study. Hydrosilylation of styrene is often plagued by competing isomer-

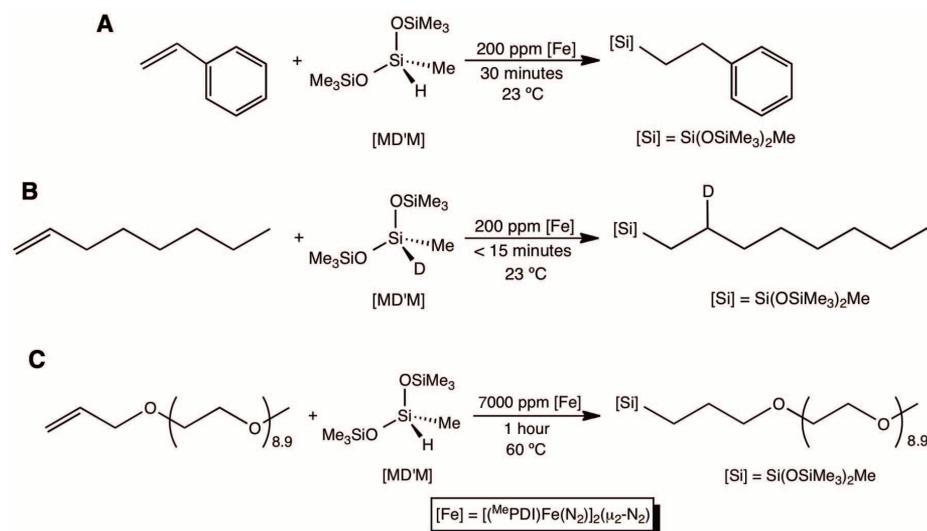
ization and sometimes favors silicon addition to the carbon closest to the aryl ring (30). Hydrosilylation of this alkene with MD'M in the presence of 200 ppm  $[(^{\text{Me}}\text{PDI})\text{Fe}(\text{N}_2)_2](\mu_2\text{-N}_2)$  exclusively furnished the anti-Markovnikov product in >98% conversion after 30 min (Fig. 2A), highlighting the preference for the iron catalyst to functionalize the terminal position of the alkene. In contrast,  $(^i\text{PrPDI})\text{Fe}(\text{N}_2)_2$  produced no turnover at 2000 ppm or higher loadings. Instead, transfer hydrogenation from one of the ligand isopropyl substituents to the substrate to yield ethylbenzene was observed (31).

To further probe the regioselectivity, we conducted a deuterium-labeling experiment for the hydrosilylation of 1-octene. If chain-running processes were competitive, deuterium would be found throughout the alkyl chain of the product. Hydrosilylation with  $(\text{Me}_3\text{SiO})_2\text{MeSiD}$  with  $[(^{\text{Me}}\text{PDI})\text{Fe}(\text{N}_2)_2](\mu_2\text{-N}_2)$  yielded the anti-Markovnikov product with deuterium incorporated only in the 2 position of the alkyl chain, demonstrating that chain running is not competitive during catalytic turnover (Fig. 2B).

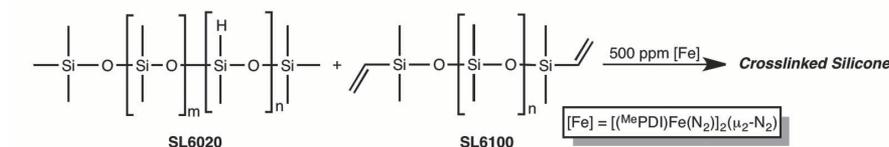
To screen the compatibility of the iron catalysts with functional groups, we studied the hydrosilylation of amino-substituted olefins, as these substrates often poison platinum catalysts. In the presence of 2000 ppm [0.03 mole percent (mol %); 200 ppm Fe metal] of  $[(^{\text{Me}}\text{PDI})\text{Fe}(\text{N}_2)_2](\mu_2\text{-N}_2)$ , the hydrosilylation of *N,N*-dimethylallylamine with MD'M reached completion in 15 min, demonstrating the potential compatibility of the bis(imino)pyridine iron catalysts with functionalized alkenes. The more sterically congested  $(^i\text{PrPDI})\text{Fe}(\text{N}_2)_2$  (2000 ppm, 0.05 mol %, 200 ppm [Fe] metal) was also active for this reaction, leading to 90% conversion in 15 min at  $23^\circ\text{C}$ .

Products arising from the hydrosilylation of methyl- and *tert*-butyl-capped allyl polyethers find application as sensory and performance enhancers in personal-care products, silicone surfactants for the stabilization of polyurethane foams, and agricultural adjuvants (5, 6, 8, 32). With industrial platinum catalysts, the reactions are conducted at  $85^\circ$  to  $100^\circ\text{C}$  and require a 10 to 30 mol % excess of polyether substrate to compensate for competing isomerization to the propenyl ether that, once formed, is unreactive toward hydrosilylation. In contrast, we observed complete hydrosilylation with a methyl-capped polyether and an equimolar quantity of MD'M in the presence of 7000 ppm of  $[(^{\text{Me}}\text{PDI})\text{Fe}(\text{N}_2)_2](\mu_2\text{-N}_2)$  (0.26 mol %; 700 ppm Fe metal), as judged by  $^1\text{H}$  NMR spectroscopy (Fig. 2C). No evidence was obtained for competing olefin isomerization. The more sterically hindered iron compound,  $(^i\text{PrPDI})\text{Fe}(\text{N}_2)_2$ , produced no turnover.

The platinum-catalyzed hydrosilylation of hydrido- and vinyl-functionalized silicone fluids is widely practiced due to the application of the resulting cross-linked silicone polymers as release coatings. Replacing platinum in this specific context is particularly attractive because the viscosity and morphology of the final product



**Fig. 2.** (A) Styrene hydrosilylation catalyzed by  $[(^{\text{Me}}\text{PDI})\text{Fe}(\text{N}_2)_2](\mu_2\text{-N}_2)$ . (B) Deuterium labeling of 1-octene hydrosilylation. (C) Hydrosilylation of an allyl polyether. The 8.9 designation refers to the average number of repeat units.



**Fig. 3.** Cross-linked silicone fluids prepared using the commercial Pt catalyst (left) and the bis(imino)pyridine iron dinitrogen compound  $[(^{\text{Me}}\text{PDI})\text{Fe}(\text{N}_2)_2](\mu_2\text{-N}_2)$  (right).

makes catalyst recovery challenging. We focused our experiments on the cross-linking of two commercial silicone fluids: SilForce SL6100 and SilForce SL6020 (Momentive Performance Materials, Waterford, NY) (Fig. 3). Addition of a toluene solution containing 1000 ppm of (<sup>18</sup>PrPDI)Fe(N<sub>2</sub>)<sub>2</sub> to a neat mixture of the two fluids at 23°C resulted in immediate cross-linking. Dissolving the iron compound in a small amount of toluene is necessary because of the low solubility of (<sup>18</sup>PrPDI)Fe(N<sub>2</sub>)<sub>2</sub> in the silicone fluids. We also observed immediate cross-linking upon addition of 500 ppm of [(<sup>18</sup>PrPDI)Fe(N<sub>2</sub>)<sub>2</sub>](μ<sub>2</sub>-N<sub>2</sub>) in toluene solution. With the more active [(<sup>18</sup>PrPDI)Fe(N<sub>2</sub>)<sub>2</sub>](μ<sub>2</sub>-N<sub>2</sub>) compound, cross-linking could be achieved over the course of 2 hours in neat silicone fluid without the addition of toluene. In each case that we studied, the resulting silicone polymer was identical to material prepared commercially using platinum catalysts. Photographs are presented in Fig. 3 for visual comparison.

Collectively, these results demonstrate the potential of Earth-abundant metal complexes to compete with more rare and more expensive precious-metal counterparts. Beyond their high activities, the iron compounds offer functional-group tolerance and, perhaps most importantly, exclusive regioselectivity that obviates the need for separation of unwanted by-products obtained in industrial processes.

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#### Supporting Online Material

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# High-Latitude Forcing of the South American Summer Monsoon During the Last Glacial

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The climate of the Last Glacial period (10,000 to 110,000 years ago) was characterized by rapid millennial-scale climate fluctuations termed Dansgaard/Oeschger (D/O) and Heinrich events. We present results from a speleothem-derived proxy of the South American summer monsoon (SASM) from 16,000 to 50,000 years ago that demonstrate the occurrence of D/O cycles and Heinrich events. This tropical Southern Hemisphere monsoon reconstruction illustrates an antiphase relationship to Northern Hemisphere monsoon intensity at the millennial scale. Our results also show an influence of Antarctic millennial-scale climate fluctuations on the SASM. This high-resolution, precisely dated, tropical precipitation record can be used to establish the timing of climate events in the high latitudes of the Northern and Southern Hemispheres.

**D**ansgaard/Oeschger (D/O) and Heinrich events have been recognized in many terrestrial and marine records, particularly from the Northern Hemisphere. First observed in oxygen isotope ratios of ice cores from Green-

land (1), the D/O cycles are interpreted as large abrupt warmings (interstadials) followed by more gradual cooling to stadial conditions. The D/O cycles are particularly well expressed in tropical Northern Hemisphere speleothem records, where cold and warm periods in Greenland are coincident with dry and wet periods, respectively, in the East Asian and Indian summer monsoons (EASM and ISM) (2–4). The presence of D/O cycles in the Southern Hemisphere, or their relation to Southern Hemisphere monsoons, has not been established, however. Heinrich events are pronounced cold intervals (~500 ± 250 years in

duration) marked by horizons of ice-rafted debris in ocean sediment cores from mid-latitudes in the Atlantic Ocean (5–7). Although an interhemispheric antiphase relation has been observed for the Heinrich (H1 to H6) events, the specific timing and duration are less well constrained because of uncertainties in ocean reservoir ages (δ) and changes in sediment accumulation rates. Here we present a high-resolution, precisely dated, speleothem reconstruction of South American summer monsoon (SASM) intensity for the Last Glacial period. This record demonstrates the presence of D/O cycles in the SASM, where an intensified SASM is associated with stadial events in Greenland. In addition, we identify millennial-scale climate events that resulted from the interplay between rapid Antarctic warming and cool North Atlantic Heinrich events. Finally, we use the signature of the major D/O cycles to propose possible constraints on the timing and duration of Heinrich events H4 and H5.

We collected stalagmite P09-PH2 from Pacupahuain Cave (11.24°S, 75.82°W; 3800 m above sea level) in the central Peruvian Andes (fig. S1). Pacupahuain Cave was formed in a Triassic dolomitic limestone massif (9) and in an area where glacial landforms are not present. P09-PH2 is a calcite stalagmite 16 centimeters tall and was collected in the cave's main gallery about 500 m from the entrance. The speleothem was halved along the growth axis and subsampled along growth layers for radiometric dating, using uranium-thorium (U-Th) techniques by

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