Spin-bearing molecules can be stabilized on surfaces and in junctions with desirable properties, such as a net spin that can be adjusted by external stimuli. Using scanning probes, initial and final spin states can be deduced from topographic or spectroscopic data, but how the system transitions between these states is largely unknown. We address this question by manipulating the total spin of magnetic cobalt hydride complexes on a corrugated boron nitride surface with a hydrogen-functionalized scanning probe tip by simultaneously tracking force and conductance. When the additional hydrogen ligand is brought close to the cobalt monohydride, switching between a correlated Kondo state, where host electrons screen the magnetic moment, and an $S = 1/2$ state, where host electrons screen the magnetic moment, and an $S = 1$ state with magnetocrySTALLine anisotropy is observed. We show that the total spin changes when the system is transferred onto a new potential energy surface that is defined by the position of the hydrogen in the junction. These results show how and why chemically functionalized tips are an effective tool to manipulate adatoms and molecules and a promising new method to selectively tune spin systems.

**INTRODUCTION**

The magnetic behavior of adatoms and single molecular magnets on surfaces is usually defined by static parameters, such as local symmetry, spin-orbit interaction, or exchange coupling with the electron bath of the host $\{1–5\}$. However, there is a widespread interest in actively controlling molecular and adatom spin states for switching applications $\{6, 7\}$. Beyond imaging and spectroscopy, scanning probes are atomically precise manipulation tools $\{8, 9\}$. When manipulation and spectroscopy operate in tandem, it is possible to observe the formation of chemical bonds and continuously tune the exchange interaction between magnetic impurities $\{10–13\}$. Tip functionalization, now routinely used to create chemically precise contacts where a molecule acts as a transducer, is one promising method to control spins $\{14–18\}$. This strategy has its roots in small-molecule adsorption on metal-bearing porphyrins and phthalocyanines $\{19, 20\}$ and capitalizes on two strengths of local probes: the ability to address specific atomic sites and the variable width of the tunnel junction. With magnetic adatoms gaining prominence as model quantum systems, it is highly desirable to understand how chemically reactive probes couple to and influence the measurement process and eventually control the resulting magnetic state.

Here, we reversibly control the total spin of cobalt hydride (CoH) spin centers adsorbed on the $h$-BN/Rh$(111)$ moiré by manipulating a single hydrogen atom with the tip of a combined scanning tunneling microscope (STM) and a noncontact atomic force microscope (AFM). As the distance $z$ between the probing tip and the CoH complex decreases, hydrogen initially adsorbed on the tip apex weakly bonds to the CoH complex, inducing rapid transitions between a correlated $S = 1/2$ Kondo state and an anisotropic $S = 1$ state. Local spectroscopy identifies a stable total spin at high and low values of the conductance, whereas intermediate conductance, dynamic switching is observed. By combining conductance-distance $[G(z)]$ and force-distance $[F(z)]$ measurements together with density functional theory (DFT) calculations, we unravel the microscopic potential energy landscapes present within the tunnel junction. We demonstrate that, by coupling a functionalized tip to an undercoordinated adatom, the reactivity of the adatom can be harnessed to drive transitions between different total spin states. The spin within the tunnel junction can therefore be actively monitored and reversibly controlled with single-atom precision.

**RESULTS**

Figure 1A shows a constant current image of CoH complexes on $h$-BN/Rh$(111)$. The lattice mismatch between the Rh$(111)$ substrate and the single monolayer of $h$-BN results in a strongly corrugated surface with 3.2-nm periodicity, on which the CoH complexes appear as bright protrusions. A clear indication of hydrogen adsorption on the tip apex is the sharp change in tip height, reduced by 20 pm (Fig. 1A, red dashes), while imaging the $h$-BN/Rh$(111)$ surface in constant current mode (21). Figure 1B shows constant current images of an individual CoH complex located near the rim-valley boundary of $h$-BN/Rh$(111)$ that is imaged with a hydrogen-functionalized tip. At low junction conductance ($G = I_d/V_S = 1.61 \times 10^{-4}$ G$0$; $G_0 = 77.48$ $\mu$S; the quantum of conductance), corresponding to relatively large tip-sample separations $z$, the increased contrast due to the hydrogen in the junction partially overlaps a CoH complex (Fig. 1B, bottom panel). As $G$ is increased, this boundary region transitions to a noise-speckled circle with a brighter appearance, that is, larger $z$ height, to compensate for an overall increase in the conductance. Given the strong $G$ dependence within this narrow range, these results hint that the observed contrast is not solely due to the local topography but is also due to mechanical and electronic changes in the junction. These images are qualitatively similar to measurements of undercoordinated metal adatoms in the presence of adsorbed hydrogen $(22, 23)$. Because the hydrogen content of the CoH$_x$ complex governs the spin state ($S$), $dI/dV$ spectroscopy was performed while varying the setpoint conductance $G$ with the tip positioned over the central region. At the lowest conductance, $G = 6.45 \times 10^{-4}$ G$0$ (Fig. 1C, bottom curve), the spectra show two symmetric steps around zero bias with increasing differential conductance. These steps originate from the inelastic spin...
measurements over CoH

type conductance range corresponds to a
d\text{I}/dV

where the topographic appearance is closely linked to the features in the

also aids in the interpretation of the STM images in Fig. 1B. The constant

current 

during the spectroscopic measurement (see also fig. S2). Differential

Note that this metastable behavior does not depend on the bias voltage

Increasing the conductance in steps of

excitations of a CoH complex with a total spin \( S = 1 \), where magneto-
crystalline anisotropy has removed the 3d-level degeneracy. Increasing

G by decreasing the tip-sample separation \( z \) results in progressively un-
stable spectra until the emergence of a stable zero bias peak at \( G = 12.9 \times 10^{-4} \text{G}_0 \), identified as an \( S = 1/2 \) CoH\(_2\) Kondo resonance (5). This

transition is fully reversible, and the initial \( S = 1 \) total spin state is re-
stored when the junction conductance is reduced (see fig. S1). We ob-

serve a metastable state, when \( G \) is between \( 8 \times 10^{-5} \text{G}_0 \) and \( 11 \times 10^{-5} \text{G}_0 \),

where the hydride complex randomly transitions between the \( S = 1 \) and

\( S = 1/2 \) states on a time scale of 100 ms. The change in tip-sample se-

paration for this conductance range corresponds to a \( \Delta z \) of less than 25 pm.

Note that this metastable behavior does not depend on the bias voltage
during the spectroscopic measurement (see also fig. S2). Differential

conductance (\( dI/dV \)) spectroscopy not only identifies the spin state but

also aids in the interpretation of the STM images in Fig. 1B. The constant

current images in Fig. 1B were obtained over a bias range (0.3 to 1.6 mV)

where the topographic appearance is closely linked to the features in the

\( dI/dV \) measurements and, therefore, at small bias voltages, is dominated

by the Kondo resonance.

To investigate the switching behavior in detail, we performed \( G(z) \)

measurements over CoH\(_x\) complexes and bare h-BN. Approaching h-BN

as well as CoH\(_x\) complexes with a bare tip reveals a strictly exponential

increase in conductance, \( G(z) = G_0 \exp(-2\kappa_c(z_0 + z)) \), where \( \kappa_c \) is

the decay rate and \( z_0 \) is the tip height at the initial setpoint conductance \( G \)

(Fig. 2A). Functionalizing the tip apex with hydrogen alters the junction

conductance characteristics, with \( G(z) \) showing a less than exponential

increase and a reduced \( \kappa_c \) compared to the data obtained with a bare

tip (Fig. 2B). This characteristic behavior is similar to the observations

of Weiss et al. (18) on a complex organic molecule with a hydrogen-

functionalized tip. However, when approaching a CoH complex with a

hydrogen-functionalized tip, \( G(z) \) closely follows the h-BN trace until

the conductance rapidly decreases by a factor of 2.5, indicating the \( S = 1 \)
to \( S = 1/2 \) transition (Fig. 2B, red) that is observed by local spectroscopy

in Fig. 1C. Therefore, the drop in conductance stems from both the di-

rect transfer of hydrogen within the junction, altering the geometry and

modifying the tunnel barrier, and the relative change in total conduct-

ance between the CoH and CoH\(_2\) complexes.

To understand the electronic structure modification in the spin-

switching process, we performed DFT calculations for various representa-
tive junction geometries (Fig. 2C). A CoH complex on h-BN exhibits a

nearly free atom–like electronic structure (Fig. 2C, i), with Stoner split 3d

levels giving it a magnetic moment of 2.0 \( \mu_B \) (without tip) (i), the second plot shows a slight magnetic moment reduction (1.6 \( \mu_B \)) due to the presence of a hydrogen-functionalized tip (ii), and the third plot shows the transition from \( S = 1 \) to \( S = 1/2 \) at close tip distances (iii). The change in Stoner splitting between majority and minority bands is schematically depicted with vertical gray arrows.

Fig. 1. Influence of hydrogen-functionalized tips on imaging and spectroscopy. (A) Constant current STM image (approximately \( 5 \times 5 \text{ nm}^2; V = -15 \text{ mV}, I = 20 \text{ pA} \), \( G = 1.72 \times 10^{-3} \text{G}_0 \)) of CoH complexes on the h-BN/Rh(111) moiré obtained with a hydrogen-

functionalized tip. Areas with enhanced contrast due to hydrogen in the junction are
circled in red. (B) Constant current STM images (1.2 \( \times \) 1.2 nm\(^2\); top to bottom: \( V = -0.3, -0.7, -1.0, -1.3, \) and -1.6 mV; \( I = 20 \text{ pA} \)) corresponding to \( G = 8.60 \times 10^{-4}, 3.69 \times \)

10\(^{-4}\), 2.58 \( \times \) 10\(^{-4}\), 1.99 \( \times \) 10\(^{-4}\), and 1.61 \( \times \) 10\(^{-4}\) \( \text{G}_0 \) of a CoH complex highlighting the

strong conductance (tip-sample distance) dependence of imaging with a hydrogen-

functionalized tip. (C) Local spectroscopy obtained on the CoH complex in (B). The tip

was centered on the bright lobe (\( G = 1.61 \times 10^{-4} \text{G}_0 \)). At \( G = 6.45 \times 10^{-4} \text{G}_0 \) (blue), a set

of double steps is observed, indicative of a spin 1 complex with magnetic anisotropy.

Increasing the conductance in steps of \( \Delta G = 0.16 \times 10^{-4} \text{G}_0 \) leads to unstable spectra

until a spin \( 1/2 \) Kondo peak emerges at high conductance (red; \( G = 1.29 \times 10^{-4} \text{G}_0 \)). All

spectra are normalized to the differential conductance at \( -10 \text{ mV}; \) normalized spectra are

offset by 0.5 arb. units, arbitrary units.

Fig. 2. Conductance-distance spectroscopy. (A) Conductance-distance, \( G(z) \), curves obtained with a bare Pt tip on h-BN (black), CoH (dashed blue), and CoH\(_2\) (dotted yellow) at a tip-sample bias of \( V = -10 \text{ mV} \). (B) Using a functionalized tip, CoH + H\(_{\text{tip}}\) (red), a conductance discontinuity, corresponding to the \( S = 1 \) to \( S = 1/2 \) total spin change, is observed at a relative height of 70 pm. The functionalized tip approaching the sub-

strate, h-BN + H\(_{\text{tip}}\) (dashed green), shows no discontinuity and has a nonexponential character. For direct comparison, the CoH \( G(z) \) measurement from (A) is plotted again (dashed blue). Inverse decay constants, \( \kappa_c \); (A) h-BN (black), 8.7 \pm 0.1 nm\(^{-1}\); CoH (dashed blue), 9.9 \pm 0.1 nm\(^{-1}\); CoH\(_2\) (dotted yellow), 9.8 \pm 0.1 nm\(^{-1}\); (B) h-BN + H\(_{\text{tip}}\) (dashed green), 6.6 \pm 0.3 nm\(^{-1}\) (0 < \( z < 70 \) pm) and 7.7 \pm 0.4 nm\(^{-1}\) (70 pm < \( z < 200 \) pm); CoH + H\(_{\text{tip}}\) (red), 6.9 \pm 0.4 nm\(^{-1}\) (0 < \( z < 70 \) pm) and 8.5 \pm 0.5 nm\(^{-1}\) (70 pm < \( z < 200 \) pm). The color-coded insets schematically depict the junction geometry. (C) Plots of

majority (left) and minority (right) spin-projected density of states (blue, d orbitals; red, sp orbitals) of an \( S = 1 \) CoH complex. The first plot shows a magnetic moment of 2.0 \( \mu_B \) (without tip) (i), the second plot shows a slight magnetic moment reduction (1.6 \( \mu_B \)) due to the presence of a hydrogen-functionalized tip (ii), and the third plot shows the transition from \( S = 1 \) to \( S = 1/2 \) at close tip distances (iii). The change in Stoner splitting between majority and minority bands is schematically depicted with vertical gray arrows.
over switching complexes and the bare h-BN. To remove the long-range forces between the extended tip and the sample, we subtract the background from the data, that is, $\Delta f = \Delta f_{\text{CoH}} - \Delta f_{\text{h-BN}}$ (see Materials and Methods and fig. S3). The $\Delta f$ is small and negative before rapidly decreasing upon approach (Fig. 3A, black). This sharp drop in $\Delta f$ coincides with a change in the $G(z)$ measurement similar to that in Fig. 2B; however, here, this feature is broadened because of averaging over the 100-pm oscillation amplitude (Fig. 3A, gray). Short-range forces, $F(z’)$, were quantified by converting $\Delta f(z)$ using the method of Sader and Jarvis (24). Before the $S = 1$ to $S = 1/2$ transition, the force between the tip and sample is weakly attractive and grows exponentially upon approach. As the hydrogen on the tip apex couples to the CoH complex, the attractive force grows steeply over a transition region of 35 pm before leveling off (Fig. 3B). The instantaneous junction conductance, $G(z’)$, is deconvoluted to remove the influence of an oscillating tip (25), revealing that the force and conductance transition regions coincide.

From the $F(z’)$ measurement, we reconstruct the one-dimensional (1D) potential energy landscape, $U(z’)$, across the spin transition by integrating $F(z’)$ (Fig. 3C). The $U(z’)$ curve shows a steep change in slope as the tip brings the hydrogen closer to the CoH complex, suggestive of a transition between potential energy surfaces. This interpretation is broadly in line with a framework recently developed by Hapala et al. (26) to describe high-resolution AFM imaging with functionalized tips. One key component of this model is that the probe particle, hydrogen in our case, not only follows the lowest potential energy surface but also undergoes relaxation within the junction. In our $U(z’)$ measurement, the kink corresponds to the relative $z’$ distance where the hydrogen on the tip apex can relax onto a lower potential energy surface. Chemically, CoH is transformed into CoH$_2$, a magnetically distinct complex with a different potential energy surface. DFT calculations show that the transition between the two distinct chemical configurations proceeds via a continuum of intermediate transition states. This intermediate regime is characterized by hydrogen on the tip sharing its bond with the tip apex and the CoH while simultaneously undergoing reorientation within the junction. In tackling this complexity, it is instructive to examine the diabatic potential energy surfaces in the limiting cases, that is, when CoH interacts with a hydrogen-functionalized tip and when CoH$_2$ interacts with a clean metallic tip. In Fig. 3D, we plot the dependence of the total energies of the two abovementioned configurations (red dash-dotted and blue dashed curves, respectively) on the

![Fig. 3. Force measurements on a switching complex.](http://advances.sciencemag.org/)

**A** Simultaneous frequency shift-distance ($\Delta f/dz$) measurements at $V = -10$ mV on a CoH $S = 1$ complex with hydrogen-functionalized tip. The spin transition, occurring at a relative height $z$ of 50 pm, is evident in both force and conductance channels. (B) Frequency shift was converted to short-range forces (black) and the conductance was deconvoluted to remove averaging over the oscillation amplitude (gray). On either side of the transition region, the deconvoluted conductance (Deconv. cond.) and force increase exponentially and can be described by the expressions $G(z) = G_0 \exp(-2z/k_BT_0 + z^2)$ and $F(z) = F_0 \exp(-2z/k_BT_0 + z^2)$, respectively. Inverse decay constants: $k_T 13.0 \pm 0.5$ nm$^{-1}$ (0 $z’ < 30$ pm) and 9.5 $\pm 0.1$ nm$^{-1}$ (70 $z’ < 200$ pm); $k_T 10.0 \pm 0.5$ nm$^{-1}$ (0 $z’ < 30$ pm) and 4.2 $\pm 0.3$ nm$^{-1}$ (70 $z’ < 200$ pm). (C) Interaction potential energy surface during the $S = 1$ to $S = 1/2$ transition (black), determined by integrating the experimental $F(z’)$ data. Dashed lines highlight the change in slope and indicate the point where a lower potential energy surface becomes accessible. Vertical dotted lines in (B) and (C) indicate the transition regime. For all curves, zero distance corresponds to the point of closest approach. (D) Simulated diabatic potential energy curves for a CoH/h-BN/Rh(111) complex approached by a hydrogen-functionalized Pt tip (blue dash-dotted curve) and a CoH$_2$ approached with a bare tip (red dash-dotted curve). The approximate adiabatic curve is shown as the gray dotted line. The reaction coordinate $d_{\text{Co-Pt}}$ is the distance between the Co and the apex Pt atoms.
DISCUSSION

We have reversibly switched the spin state of cobalt hydride complexes in a tunnel junction by using the hydrogen on the tip apex as a tunable ligand. During the total spin change, a transition region exists where the hydrogen can occupy two nearly equivalent sites separated only by a negligible barrier. As the junction conductance is altered, site equivalence is removed, and the tip displacement shifts the system to a preferred site. Beyond total spin, interactions with the tip determine how the cobalt spin couples with the host electron bath and whether a correlated Kondo state emerges. The relative stability of the double potential well and the possible occurrence of correlations are expected to be dependent on the materials used and the reactivity of the adsorbed molecule on the tip and the undercoordinated adatom. Reconstructing the 1D potential energy landscape shows that chemical transformation within the junction is responsible for the change of the total spin. Our measurements highlight how tip functionalization can influence the spin under investigation and suggests that they may be used to tailor molecular spins in ways difficult to achieve through traditional chemical synthesis.

MATERIALS AND METHODS

The clean Rh(111) surface was prepared by multiple cycles of argon ion sputtering and annealing to 1100 K in an ultrahigh vacuum chamber. During the final annealing cycle, borazine (B₃N₃H₆) gas was exposed to the hot sample at a pressure of 1.2 × 10⁻⁶ mbar for about ~2 min, resulting in a monoatomic layer of h-BN. Subsequently, the sample was cooled down (~20 K), and cobalt was deposited via an electron beam evaporator. Because hydrogen is the predominant component of the residual gas background, it is responsible for the formation of the cobalt hydride complexes. STM/AFM experiments were performed on a homebuilt instrument operating in ultrahigh vacuum at a base temperature of 1.1 K. All spectroscopic (dI/dV) measurements were performed by adding a small sinusoidal voltage (V_mod = 0.2 mV, f_mod = 600 to 800 Hz) to the bias voltage V and using an external lock-in amplifier. We used V = −10 mV to adjust the conductance G before recording dI/dV curves by varying V at constant z, as well as to record G(z) and Δf(z) curves at constant V. Hydrogen pickup occurred fortuitously as the experiments went on, for example, during the approach of an initial CoHₓ (x = 1 to 2) complex with a nonfunctionalized tip. Hydrogen-terminated tips were initially identified by features such as enhanced contrast in constant current imaging and then verified by the characteristic nonexponential behavior in G(z) measurements (Fig. 2B, green).

The quartz tuning fork has a resonance frequency of f₀ = 29.077 Hz and a quality factor of approximately 10,000. Oscillation amplitudes of 100 pm were used. For the frequency shift curves, Δf(z), the tip was positioned above the CoH complex with the oscillating tuning fork. The feedback loop was disabled, and the oscillating tip then approached 200 to 300 pm toward the sample and back. Immediately after completion, a retract curve was obtained by moving 2000 pm away from the surface (see fig. S3). When this sequence was completed, the tip was moved at constant height to the bare h-BN, and Δf_BN was obtained. The frequency shift due to short-range forces was obtained by taking the difference Δf = Δf_{CoH} − Δf_{BN}. We distinguish between time-averaged signals at tip heights z and deconvoluted (instantaneous) signals at tip heights z’.

First-principles calculations were carried out in a manner consistent with the calculations used in our previous work (5). Briefly, a DFT approach, based on the projector augmented wave method (27) and a plane wave basis set (28), was used as implemented in the Vienna Ab initio Simulation Package (29). Exchange and correlation were treated with the gradient-corrected functional as formalized in PBE (Perdew, Burke, Ernzerhof) (30). On-site Coulomb interaction corrections were accounted for in the framework of the LSDA+U (local spin density approximation including Hubbard U) formalism, as introduced by Dudarev et al. (31). The considered geometry of the system was identical to the one introduced in the study by Jacobson et al. (5), that is, a Rh(111) surface was simulated by five Rh layers, on top of which an h-BN sheet was deposited (considered to be commensurate for computational feasibility reasons). A CoH complex was residing on top of an N atom of the h-BN sheet. The tip was simulated by a Pt pyramid of four atoms attached to an Rh surface. Before the tip approach simulation, the tip and the sample were allowed to relax. After placing the tip in the vicinity of the CoHₓ complex, the CoHₓ complex and the apex atom of the tip (as well as the attached hydrogen atom, where appropriate) were allowed to relax again, assuming an equilibrium static configuration. A full relaxation of the tip and the h-BN atoms around the CoHₓ complex was tested and not found to introduce any change to the results above the calculation error level. In the experimentally relevant case of a CoH complex being approached with a singly hydrogenated tip, we are thus left with four atoms allowed to relax in three dimensions, amounting to a 12D configuration space. However, in effect, both the apex Pt and the Co atoms were found to experience only vertical relaxations, which, according to our tests, result in a minor quantitative change of the total energies and magnetic moments. This complies with our understanding of the mechanism of CoHₓ complex spin switching, the latter being governed by the Co–H bonding, which, in turn, is altered through the rearrangement of the hydrogen atoms. To underline this fact, the calculation results presented in Fig. 3D and fig. S6 were obtained in a diabatic fashion, meaning that the initial relative orientation of the CoHₓ and the TipHₓ atoms were kept frozen and that only the distance between the tip and the sample (characterized by the distance d between Co and apex Pt atoms) (see fig. S4) was varied. For hydrogen adsorption and transfer energies as well as the adiabatic transition calculation, the junction was allowed to relax.
REFERENCES AND NOTES


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Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

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