The long-term depletion trend is obscured in the Mesozoic part of the data (white background in the second figure) because it was unusually warm (i.e., lower $\delta^{18}O$) in the Cretaceous. Age depletion is not peculiar to biogenic carbonates but is seen in vertebrate phosphates as well (see the second figure).

Compensating for this trend would lower the warmest fish growth temperature to $26° \pm 2°C$, and ichthyosaurian T_b to about $24° \pm 2°C$. The values agree with our knowledge of marine vertebrate physiology (excluding mammals and birds): The T_b of homeothermic marine vertebrates, such as tunas and leatherback turtles, is about $20°$ to $25°C$ (8, 9). A growth temperature of $26°C$ occurs among fish living in the warmest seas today.

The conclusion of homeothermy was not affected by this bias removal. Although future scrutiny is necessary, the following picture emerges. At a T_a of $10°C$, all three groups had a T_b of about $24°C$. As the T_a rose to $36°C$, mosasaur T_b increased to $36°C$, whereas the other two groups maintained an almost constant T_b. Large cruisers among living nonmammalian marine vertebrates red muscles tuned for an in vivo temperature centered around $25°C$ (9, 10).

All three groups had a higher T_b than co-occurring fish by about $5°$ to $20°C$, with the exception of Triassic ichthyosaurs. This suggests that they had heat conservation systems such as blubber layers and specialized blood circulation. Perhaps some of them were endothermic (i.e., having elevated resting metabolic rates and generating extra heat inside their bodies). However, no living reptile (other than birds) is known to be endothermic. Even homeothermic leatherback turtles are not endothermic but gigantothermic [i.e., they maintain T_b by virtue of large body size and insulation], sometimes more than $20°C$ above T_a (8), without extra internal heat generation. The warmest marine reptiles described by Bernard et al. were giants, such as the mosasaur *Tylosaurus*, whereas a co-occurring smaller mosasaur was about $5°C$ colder. Considering this and the overheating tendency of mosasaurs, they may have been gigantothermic. Perhaps plesiosaurs and ichthyosaurs were regional endotherms, as are tunas and lamnid sharks (9).

The conclusions of Bernard et al. only apply to Jurassic and Cretaceous marine reptiles, given the data range. By that time, ichthyosaur and plesiosaur lineages had completed their adaptation for cruising, with ichthyosaurs having semi–crescent-shaped tail flukes and plesiosaurs two pairs of rigid and pointed flippers (see the first figure). When did homeothermy evolve in these lineages?
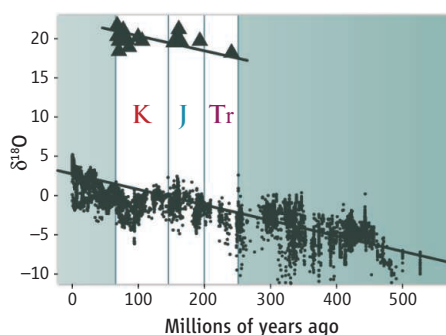
Similarity in $\delta^{18}O$ depletion trends between biogenic carbonate (triangles) and phosphates (dots). Lines represent standardized major axis regression lines as implemented in the smatr package of software platform R (13). Data were taken from (4) and (7). K, Cretaceous; J, Jurassic; Tr, Triassic.

They lived on land until the Early Triassic and, given the physiology of current land-living reptiles, it is unlikely that the land ancestors were homeothermic. The transition may have occurred in the Late Triassic, as these reptiles thrived through changing environments after their initial aquatic adaptation.

Evolution of a tuna-shaped body plan in ichthyosaurs, which enabled them to cruise the seas, was correlated with a decrease in coastal habitats in the Middle to Late Triassic (11). Most coastal marine reptiles became extinct as their habitats were lost, but cruising ichthyosaurs prospered. If homeothermy in ichthyosaurs evolved in conjunction with cruising, then there is an opportunity to clarify environmental effects on evolution. Evolutionary triggers for homeothermy are generally difficult to decipher (12), yet comparisons of the evolutionary records of marine reptiles and fish may illuminate common environmental factors.

References and Notes
1. J. A. Massare, *J. Vertebr. Paleontol.* **7**, 121 (1987).
2. R. Motani, *Evol. Educ. Outreach* **2**, 224 (2009).
3. J. A. Massare, in *Mechanics and Physiology of Animal Swimming*, L. Maddock, Q. Bone, J. M. V. Rayner, Eds. (Cambridge Univ. Press, Cambridge, 1994), pp. 133–149.
4. A. Bernard et al., *Science* **328**, 1379 (2010).
5. V. D. Buffrénil, J. Mazin, *Paleobiology* **16**, 435 (1990).
6. R. Motani, *Nature* **415**, 309 (2002).
7. J. Veizer, Y. Godderis, L. M. François, *Nature* **408**, 698 (2000); updated data available from www.science. uottawa.ca/~veizer/isotope_data/.
8. B. P. Wallace, T. T. Jones, *J. Exp. Mar. Biol.* **356**, 8 (2008).
9. J. B. Graham, K. A. Dickson, *J. Exp. Biol.* **207**, 4015 (2004).
10. D. Bernal et al., *Nature* **437**, 1349 (2005).
11. R. Motani, *Sociol. Pap.* **14**, 147 (2008).
12. K. A. Dickson, J. B. Graham, *Physiol. Biochem. Zool.* **77**, 998 (2004).
13. D. I. Warton et al., *Biol. Rev. Camb. Philos. Soc.* **81**, 259 (2006).

APPLIED PHYSICS

Pulling Apart Molecular Magnetism

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Mechanical control can be used to probe and tune the magnetic properties of single molecules.

A single molecule constitutes the ultimate nanometer-scale object through which electronic transport can take place. Being so small, molecules share many characteristics with atoms, such as discrete quantized energy spectra and angular momentum, yet at the same time are large enough to be mechanically deformed and chemically attached to metallic leads with which they can exchange electrons. Can these mechanical and exchange interactions be controlled and, if so, what new phenomena arise? On page 1370 of this issue, Parks et al. (1) show how magnetism and quantum many-body phenomena can be tuned by precise mechanical manipulation of single molecules.

Quantum mechanics tells us that electrons confined within a potential "box" can have a discrete set of allowed energies. Such a discrete energy spectrum (the energy levels and the spacing between them) depends on the strength of the confining potential and the boundary conditions imposed on the electron wave functions. For symmetric potentials, such as the Coulomb potential from a nucleus, the quantum energy states exhibit orbital degeneracies (i.e., the s, p, d… atomic shells). Pauli's exclusion principle dictates that at most two electrons with total spin zero can occupy a given energy state. But for orbitally degenerate states, two or more electrons may align their spins by occupying different states, minimizing their Coulomb repulsion— as is exemplified by Hund's rule. Orbital degeneracies are of fundamental importance for the existence of atoms with large magnetic moments (spin, $S \geq 1$) and play an important role in molecular magnetism.

Surrounding such magnetic atoms with other atoms and ligands to form a molecule alters the boundary conditions for the quan-

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tum box. This can lead to a splitting of the different orbital and spin states, depending on the symmetry properties of the atom's environment, and in turn results in a modification of the magnetic properties of the entire system. Parks *et al.* investigate the magnetic states of individual $S = 1$ molecules placed between two electrodes in a metal break junction. By stretching the electrodes, they explore the resulting symmetry-breaking effects of this mechanical action on the conduction properties through the molecule. They focus on the magnetic anisotropy of the molecules—how the energy differences among the different S_z states ($S_z = 0, \pm1$) change for different degrees of stretching.

Now, getting to know the spin configuration of an individual molecule in a changing environment is nontrivial, but here is where quantum many-body physics comes to the rescue. A well-known correlated electronic transport phenomenon, called the Kondo effect (*2*), is exquisitely sensitive to the presence of spin and orbital degeneracies. In its simplest incarnation—the spin ½ Kondo effect—an isolated spin-½ magnetic impurity (e.g., a single electron) is antiferromagnetically screened by the conduction electrons in a host metal. The net result is the formation of a singlet state (a spin-up and spin-down combination, with $S = 0$) between the metallic leads and the magnetic impurity. The Kondo effect results in a continuous exchange of spin-up and spin-down electrons between the leads and the magnetic impurity (*3, 4*). This exchange enables highly efficient electronic transport through the impurity at zero bias, that is, a single peak in differential conductance (dI/dV) at a source-drain bias (V) of zero (see the figure, panel A). The binding energy of this correlated state is characterized by a temperature scale called the Kondo temperature, T_K. Key to this process is that the spin-½ impurity state

is twofold degenerate (both $S_z = \pm½$ spin orientations have the same energy). Creating an energy splitting between these spin states by, for example, applying a magnetic field, leads to a splitting of the Kondo resonance as soon as the splitting exceeds $\sim T_K$.

At zero temperature, a number $2S$ of channels in the leads are required to completely screen an isolated spin S (*5*). In the case of a spin-½ impurity, this means just one screening channel, which typically consists of combinations of conducting states in the two metallic leads to which the molecule is coupled. For larger spin, for example, $S = 1$, things get trickier. Each of the two screening channels ($2S = 2$) will have in general a different coupling to the magnetic impurity. Because the Kondo temperature associated with each screening channel is an exponential function of the coupling strength, this means that there will be two Kondo temperatures, T_{K1} and T_{K2}, which can be very different. Therefore, in general there will be a temperature regime $T_{K1} < T < T_{K2}$, in which only one out of the two spin-½ degrees of freedom in the molecule will be screened. This results in the underscreened Kondo effect, which has a very different temperature dependence than the ordinary $S = ½$ Kondo effect (*6*). The strategy then is to measure the differential conductance of your molecular device. If you see a Kondo peak, then its temperature dependence reveals the spin of the molecule.

The theoretical predictions for this $S = 1$ underscreened Kondo effect were recently confirmed in a different experiment (*7*). Parks *et al.* report that they can lift the degeneracy (separate the levels) of the three triplet states by mechanically pulling apart the metal leads connected to the molecule. Such molecular stretching results, in this case, in a $S_z = 0$ singlet ground state, with the two other triplets ($S_z = \pm1$) being higher in energy by an amount

called the magnetic anisotropy energy, D (see the figure, panel B). Because the stretching can be controlled with subangstrom precision, the anisotropy energy is exquisitely tunable. Once the energy splitting is comparable to T_K, the degeneracy is broken such that the Kondo effect ceases to occur. Parks *et al.* observe a gradual splitting of the Kondo conductance peak as the distance between the electrodes is varied, in agreement with prediction.
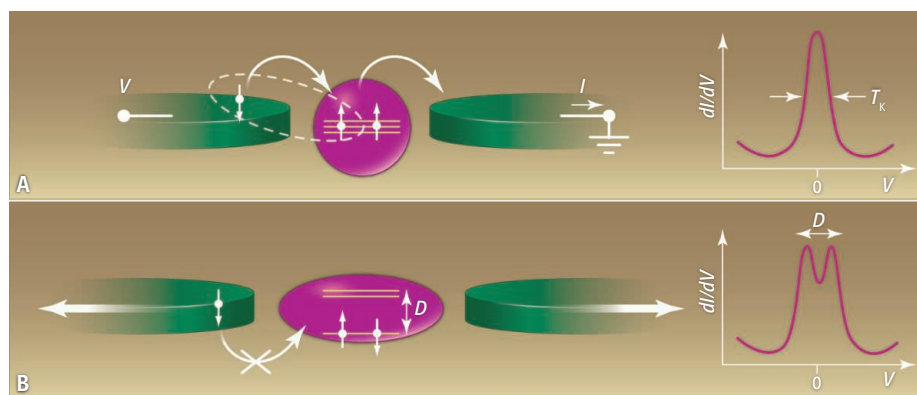
The Kondo effect has been used as a spectroscopic tool to study magnetic anisotropy in magnetic atoms connected to an environment (*8*). However, in these previous studies the atoms had a half integer spin ($S = 3/2$) for which time reversal symmetry guarantees partial spin degeneracy at zero magnetic field, and therefore a single, unsplit Kondo peak at zero magnetic field. The study by Parks *et al.* thus constitutes the case where a Kondo effect associated with a magnetic atom can be tuned by purely mechanical means, resulting in a new degree of control to investigate Kondo resonances and splittings at zero magnetic field. Moreover, having two independent knobs to tune the energy spectrum—mechanical pulling for the anisotropy and magnetic field for the Zeeman splitting—they confirm the theoretically expected behavior for the Kondo resonance peak splitting under simultaneous magnetic field and mechanical stretching.

The results by Parks *et al.* show that the Kondo effect, one of the most researched quantum many-body phenomena in strongly correlated physics, continues to surprise in all its variations (spin, orbital, multichannel, and here underscreened), and now too as a superb spectroscopic tool for nontrivial interrogations of the magnetic behavior of individual molecules. The ability to mechanically tune the magnetic anisotropy of individual molecules provides the opportunity to systematically investigate and theoretically compare quantum chemistry models, which will enormously broaden our knowledge of molecular magnetism. Beyond the fundamental science level, it may play an important role in the use and manipulation of nanoscale magnets for spintronics and quantum information processing applications.

Magnetism on the pull. (**A**) For the unstretched molecule, the three triplet states are degenerate, leading to a Kondo peak in dI/dV at $V = 0$. (**B**) Mechanically stretching the molecule splits the triplet states' degeneracy, thus leading to a controllable split of the Kondo peak, as studied by Parks *et al.*

References and Notes
1. J. J. Parks *et al.*, *Science* **328**, 1370 (2010).
2. L. Kouwenhoven, L. Glazman, *Phys. World* **14**, 33 (2001).
3. D. Goldhaber-Gordon *et al.*, *Nature* **391**, 156 (1998).
4. S. M. Cronenwett *et al.*, *Science* **281**, 540 (1998).
5. P. Nozieres, A. Blandin, *J. Phys.* **41**, 193 (1980).
6. A. Posazhennikova, P. Coleman, *Phys. Rev. Lett.* **94**, 036802 (2005).
7. N. Roch *et al.*, *Phys. Rev. Lett.* **103**, 197202 (2009).
8. A. F. Otte *et al.*, *Nat. Phys.* **4**, 847 (2008).
9. I acknowledge useful discussions with R. C. Ashoori and D. Goldhaber-Gordon.