Dihydrogen, H$_2$, exists as two allotropes or nuclear spin isomers: a nuclear singlet state with antiparallel (i.e., nuclear spins, termed para-hydrogen (pH$_2$)), and a nuclear triplet state with parallel (i.e., nuclear spins, termed ortho-hydrogen (oH$_2$)).

According to the Pauli Principle, singlet pH$_2$ is required to occupy even rotational states ($J = 0, 2, 4, ...$) and triplet oH$_2$ odd rotational states ($J = 1, 3, 5, ...$). Since $J = 0$ is the lowest rotational level of H$_2$, pH$_2$ is the ground rotational state and oH$_2$ a rotationally excited state. The energy gap between the $J = 0$ and $J = 1$ rotational states is 120 cm$^{-1}$ (0.343 kcal mol$^{-1}$). The equilibrium mixture at any given temperature is termed eH$_2$. At room temperature (RT), triplet oH$_2$ dominates at equilibrium ($e$H$_2$ = 75% oH$_2$/25% pH$_2$) because of its higher statistical weight and the small energy gap between the two rotational levels.

The two allotropes of hydrogen, oH$_2$ and pH$_2$, may be quantitatively incarcerated into C$_{60}$ to form the endofullerene guest/host complexes oH$_2$@C$_{60}$ and pH$_2$@C$_{60}$, respectively. We have developed$^5$ the following procedure for producing samples of pH$_2$-enriched H$_2$@C$_{60}$ in which the incarcerated H$_2$ spin isomers are not in spin equilibrium at RT: (1) adsorbing a sample of eH$_2$@C$_{60}$ on the external surface of NaY zeolite at RT; (2) cooling the sample to 77 K; (3) immersing the sample in liquid oxygen at 77 K, thereby converting the sample to a paramagnetic nitroxide, a “magnetic switch” for forward conversion (eH$_2$@C$_{60}$ → pH$_2$@C$_{60}$) at 77 K and back conversion (pH$_2$@C$_{60}$ → eH$_2$@C$_{60}$) at RT would be available. We describe the design and demonstration of such a magnetic switch based on the reversible nitroxide/hydroxylamine system$^6$ of H$_2$@C$_{60}$ in order to determine the effect of substitution on the forward and back conversions of the incarcerated spin isomers of H$_2$. Figure 1a shows the initial and final $^1$H NMR spectra of $^1$H$_2$@I that was put through the enrichment procedure described above. The black curve corresponds to the initial sample of eH$_2$@I. The signal at -4.4 ppm corresponds to the $^1$H signal from eH$_2$@I, and the other three signals correspond to the $^1$H signals from HD$_2$@I (the triplet results from the coupling of $^1$H with $^2$H).$^7$ The red curve corresponds to the $^1$H NMR signals after conversion. Clearly, the proportion of oH$_2$@I relative to HD$_2$@I decreased as expected: the signal intensities are consistent with a 50%/50% mixture of oH$_2$@I/pH$_2$@I, corresponding to $^1$H$_2$@I. At RT, the back conversion rate of $^1$H$_2$@I to eH$_2$@I without a spin catalyst is similar to that of $^1$H$_2$@I to eH$_2$@C$_{60}$ (see Table 1), showing that the substitution by itself does not significantly modify the rate of the back conversion.

$^1$H NMR analysis of the forward conversion of (a) eH$_2$@I (black curve) to $^1$H$_2$@I (red curve) and (b) eH$_2$@I (black curve) to $^1$H$_2$@I (red curve) in CDCl$_3$.

The H$_2@C_{60}$ sample was cooled to 77 K for several hours according to the usual procedure, and then the NMR spectrum was recorded as

**Figure 1.** $^1$H NMR analysis of the forward conversion of (a) eH$_2$@I (black curve) to $^1$H$_2$@I (red curve) and (b) eH$_2$@I (black curve) to $^1$H$_2$@I (red curve) in CDCl$_3$.
quickly as possible after the sample was warmed to RT. Within the fastest workup possible (90 s), no spin enrichment was observed [in Figure 1b, the final H signals (red and black curves) are indistinguishable]. We hypothesize that the paramagnetic nitrooxide substituent of H2@2 is such an effective spin catalyst that at RT it causes a rapid back conversion of *pH2@2 produced at 77 K to eH2@2 during the workup of the sample.

To test the hypothesis that spin enrichment to *pH2@2 occurs but is rapidly reversed to eH2@2 during workup, we synthesized a diamagnetic “masked” nitroxide, 2H3@3 (Chart 1). In addition, we expected that eH2@2 would be regenerated by oxidation of 2H3@3, creating a reversible magnetic switch for interconverting incarcerated nuclear spin isomers.

The broadened NMR (Figure 2a) and ESR (Figure S1a in the Supporting Information) spectra of the initial sample are consistent with those expected for paramagnetic eH2@2. Treatment of the sample with phenylhydrazine resulted in the conversion of paramagnetic eH2@2 to diamagnetic eH2@3. As expected, the resulting NMR signals were sharpened (Figure 2b) and the ESR signal disappeared (Figure S1b), consistent with essentially quantitative conversion of eH2@2 into eH2@3. Treatment of the eH2@3 with Cu(OAc)2 produced the NMR and ESR spectra of eH2@2, demonstrating the reversible conversion of eH2@3 back to eH2@2 in >95% yield.

The hypothesis concerning the lack of a net conversion when eH2@2 is cycled to 77 K and back to RT (Figure 1b) could be tested next, since eH2@3 is a “caged” diamagnetic analogue of eH2@2. The strategy to test the hypothesis was to convert eH2@3 to *pH2@3 at 77 K (analogous to the result for eH2@1 in Figure 1a), return the sample to RT, “uncage” the nitroxide to produce the paramagnetic *pH2@2, and determine the extent of conversion.

The specific execution of the strategy for testing the hypothesis was as follows: First, treatment of eH2@3 under the forward conversion conditions (NaY/77 K/liquid O2) was expected to cause conversion of eH2@3 to a sample of enriched *pH2@3 that would be stable to back conversion at room temperature. Treatment of *pH2@3 with Cu(OAc)2 at room temperature would generate enriched *pH2@2. If the hypothesis of rapid interconversion of the nuclear spin isomers of *pH2@2 is correct, then at RT, that portion of the sample that was oxidized to *pH2@2 would be rapidly converted to eH2@2.

The results of applying this strategy are shown in Figure 2. The 1H NMR spectrum of the initial sample of eH2@3 is shown in Figure 2b.

The intensity of the H2 signal relative to the integrated HD signal is a measure of the oH2/pH2 ratio and corresponds to the expected 75%/25% mixture of oH2/pH2 (eH2 at RT). After the forward conversion procedure, the 1H NMR showed that the sample was a mixture of H2@3 and H2@2 (Figure 2c), demonstrating that some degree of oxidation of H2@3 occurred, presumably during the treatment with O2 during the workup. Comparison of the 1H NMR signals (Figure 2d) shows that eH2@3 was indeed enriched in pH2 while eH2@2 was not. The results can be interpreted as follows: (1) some (∼25%) of the H2@3 was oxidized to H2@2 during the procedure; (2) the H2@3 that survived oxidation was enriched in pH2; (3) H2@2 was not enriched in pH2; and (4) the concentration of H2@2 in the sample was insufficient to serve as a bimolecular catalyst for the back conversion of *pH2@3. These results demonstrate convincingly that the H2@3/H2@2 system can act as a reversible switch that interconverts the incarcerated oH2/pH2 nuclear spin isomers.

These results show that the rate of nuclear spin interconversion of encapsulated H2 can be markedly increased by attaching the paramagnetic catalyst to the cage. Furthermore, comparison of the catalyzed lifetime of H2@2 (<90 s) with the uncatalyzed lifetime of ∼7.5 days (6.5 × 10^5 s) for H2@1 (Table 1) demonstrates that the rate of back conversion may be varied by >4 orders of magnitude by turning the catalyst on and off.

We are attempting to couple the ability to control the rate of conversion with the generation of nuclear polarization of the oH2 produced by the interconversion. These results have potential for magnetic resonance imaging applications employing fullerenes containing H2 as an imaging agent and for the application of the nitroxide and H2 components of H2@2 for dynamic nuclear polarization.

Acknowledgment. The authors thank the National Science Foundation for its generous support through Grant CHE 07-17518.

Note Added after ASAP Publication. The structures of the fullerene derivatives were corrected on February 25, 2010.

Supporting Information Available: Synthesis and experimental details, including EPR analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

Table 1. Relative Rates of para–ortho Conversion and Lifetimes of H2, H2@C60, H2@1, and H2@2 at RT

<table>
<thead>
<tr>
<th>Conversion</th>
<th>Rate Constant (s^-1)</th>
<th>Lifetime (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>*pH2 → eH2</td>
<td>∼1</td>
<td>&gt;10^6</td>
</tr>
<tr>
<td>*pH2@C60 → eH2@C60</td>
<td>∼1</td>
<td>&gt;10^6</td>
</tr>
<tr>
<td>*pH2@1 → eH2@1</td>
<td>∼1</td>
<td>&gt;10^6</td>
</tr>
<tr>
<td>*pH2@2 → eH2@2</td>
<td>&gt;7200</td>
<td>&lt;90</td>
</tr>
</tbody>
</table>

* Data from ref 10. b In deoxygenated 1,2-dichlorobenzene-d4.

The intensity of the H2 signal relative to the integrated HD signal is a measure of the oH2/pH2 ratio and corresponds to the expected 75%/25% mixture of oH2/pH2 (eH2 at RT). After the forward conversion procedure, the 1H NMR showed that the sample was a mixture of H2@3 and H2@2 (Figure 2c), demonstrating that some degree of oxidation of H2@3 occurred, presumably during the treatment with O2 during the workup. Comparison of the 1H NMR signals (Figure 2d) shows that eH2@3 was indeed enriched in pH2 while eH2@2 was not. The results can be interpreted as follows: (1) some (∼25%) of the H2@3 was oxidized to H2@2 during the procedure; (2) the H2@3 that survived oxidation was enriched in pH2; (3) H2@2 was not enriched in pH2; and (4) the concentration of H2@2 in the sample was insufficient to serve as a bimolecular catalyst for the back conversion of *pH2@3. These results demonstrate convincingly that the H2@3/H2@2 system can act as a reversible switch that interconverts the incarcerated oH2/pH2 nuclear spin isomers.

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(1) Parkas, A. Orthohydrogen, Parahydrogen and Heavy Hydrogen; Cambridge University Press: Cambridge, U.K., 1935; Chapter II and Chapter IV, p 76.
(7) In these experiments, HD@1 served as an internal reference.