



Figure 1 | The ruthenium(II) pincer system from Milstein *et al.*¹ is compared with a general scheme for artificial photosynthesis. **a**, When **1** is heated in water at 100 °C for a prolonged time it releases hydrogen. Water is picked up and complex **2** is formed in several steps. The two hydroxo groups form hydrogen peroxide (H_2O_2) under near-ultraviolet (UV) light, and the complex returns to **1** after uptake of water. Molecular oxygen is formed in a secondary disproportionation reaction of H_2O_2 . **b**, In a system for artificial photosynthesis, light is captured by a photoactive centre (S). The absorption of visible-wavelength photons results in charge separation and subsequent electron transfer to a reductive catalyst (A) where protons are reduced to hydrogen. The oxidized photoactive centre is reduced from an oxidative catalyst (D) where water is oxidized to molecular oxygen and protons. Both catalytic reactions, at A and D, are multi-electron and multi-proton reactions. Several candidates for A and D are mentioned in the text.

In contrast to Milstein and colleagues' system¹, this builds on electron transfer reactions between separate light-absorbing and catalytic units. All steps are driven by visible light. Moreover, the water-oxidizing and hydrogen-producing reactions should be performed at separate catalytic sites. Milstein and co-workers instead drive all their reactions at a single site, but temporarily separated in consecutive reaction steps under different reaction conditions. The chemistry they present involves less than one turnover. It is also driven in one thermal and one photolytic step, both of which are inefficient and very slow. The energy conversion yield of this combined energy input into hydrogen is also unclear at present. The strength in the report is instead the interesting, thought-provoking mechanism involving hydrogen release and water splitting in an intramolecular reaction

— connecting the work well to the efforts to manage artificial photosynthesis.

Developments of artificial photosynthesis build on photosynthetic principles of light-induced charge separation and catalysis in metal centres^{3,4}. The management of photochemical reactions and light-driven multistep electron transfer is crucial. At present a key component is to develop catalysts that can oxidize water efficiently using light energy^{5,6}. If this could be accomplished, artificial photosynthesis for fuel production from solar energy and water might be achieved. However, this is easier said than done. Several aspects need to be met by a catalyst for its future large-scale use. One critical factor is that the elements involved are abundant and environmentally friendly. Here ruthenium-based catalysts, whether they are multinuclear^{4,7} or single metal, will come up short due to the low abundance of ruthenium.

Instead, catalysts containing abundant metals need to be investigated. Photo-oxidizable biomimetic manganese complexes^{2,3} (copying photosystem II), cobalt systems on surfaces⁸ (already quite well functioning) and even iron systems⁹ are interesting candidates. Moreover, the more rapid ligand-exchange kinetics of these first-row transition metals promises much higher catalytic rates compared with heavier elements. Similar arguments hold for the reduction of protons to hydrogen. There are many diiron complexes mimicking key features in natural hydrogenases that are catalytically functional at very low redox potentials^{10–12}. Furthermore, several nickel and cobalt systems^{13–15} show promise; some of them can even be driven by light using molecular photosensitizers¹³ (analogous to the upper half in Fig. 1b). Detailed studies of natural enzymes, synthetic analogues and non-natural catalysts are important for meeting the grand challenge of efficiently splitting water using solar energy. □

Leif Hammarström and Stenbjörn Styring are in the Department of Photochemistry and Molecular Science, Ångström Laboratory, Box 523, Uppsala University, SE-751 20 Uppsala, Sweden.
e-mail: Leif.Hammarstrom@fotomol.uu.se;
Stenbjorn.Styring@fotomol.uu.se

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ERRATUM

Table manners

Michelle Franci

Nature Chemistry **1**, 97–98 (2009); corrected after print 5 May 2009.

In Fig. 1 of the version of this Thesis originally published, the element directly to the left of Bk was mistakenly written as Th, whereas it should have been Tb. This has been corrected in the HTML and PDF versions of the Thesis, along with a typing error in 'Transition'.