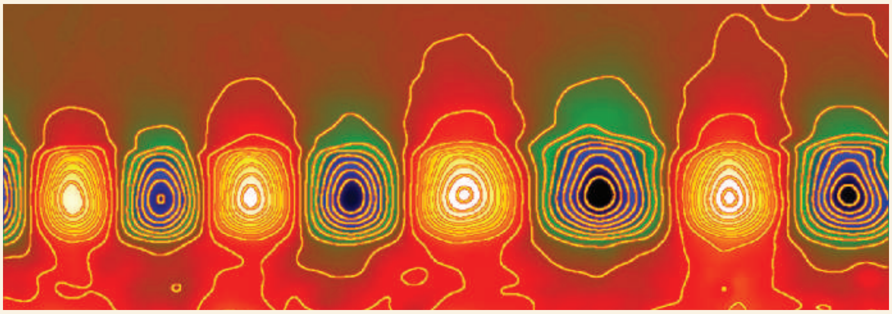
ELECTRON HOLOGRAPHY

Measuring magnetism



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Memory devices containing hard disk drives depend on the magnetic interaction between the reading and recording head and the data bits of the storage material. With data density continually increasing, understanding these materials and their interactions on an ever-decreasing scale becomes more and more important.

Now, Aurélien Masseboeuf and colleagues have used electron holography to quantitatively examine the nanoscale magnetic flux distribution in a magnetic film (pictured; *Nano Lett.* doi:10.1021/nl900800q; 2009). The film consists of ordered and disordered domains of iron–palladium on magnesium oxide. Electron holography can separate the magnetic and electrostatic contributions in the reconstructed phase, so simply inverting the sample means the electrostatic component can be removed.

Masseboeuf and colleagues observed that the magnetic domains in the ordered FePd phase were flattened near to the disordered layer, as can been seen at the bottom of the image. Compared with a calculated model, the walls between domains were thicker. The magnetic flux could be accurately measured inside and outside the sample, so the stray field can be related to the magnetization within the domains. These stray fields are the bit information for the reading heads, so this level of understanding should aid the development of improved magnetic data storage media.

NEIL WITHERS

GOLD CATALYSIS

Carbene or cation?

The exact nature of the gold–carbon bond formed during homogeneous gold catalysis has recently attracted a lot of interest and is somewhat controversial. Now a study of the bonding and trends in reactivity of various gold complexes offers new insights into whether such structures can be defined as gold-stabilized cations or gold carbenes.

Antonio M. Echavarren

Chemists communicate using molecular formulae that comprise a high level of abstraction as well as unavoidable simplifications. Certain aspects of aesthetics and fashion have also had an impact on the way complex chemical entities are represented — as can be easily seen when comparing publications and textbooks of the forties and fifties with those of today. This has occasionally resulted in the sacrifice of chemical rigour.

Chemists are aware that benzene is not 1,3,5-cyclohexatriene (**1**) with alternating single and double bonds because of Kekulé's work in the nineteenth century, but we still prefer this representation to the symmetrical structure **2** (Fig. 1a). Similarly, for the famous and controversial 2-norbornyl carbocation, picture **3** (ref. 1) more precisely highlights the nature of the 3-centre-2-electron-bond with a bridged hypercoordinate carbon atom, but it is more often drawn simply as **4** (Fig. 1b).

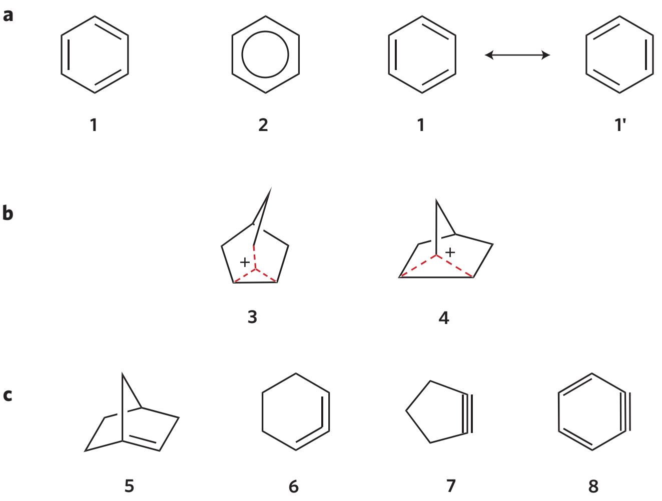

Figure 1 | Comparing preferred chemical structure representations. Different representations of **a**, benzene (**1** and **2**) and **b**, of the non-classical norbornyl carbocation (**3** and **4**). **c**, Conventional drawings of 1-norbornene (**5**), cyclohexa-1,2-diene (**6**), cyclopentyne (**7**) and benzyne (**8**).

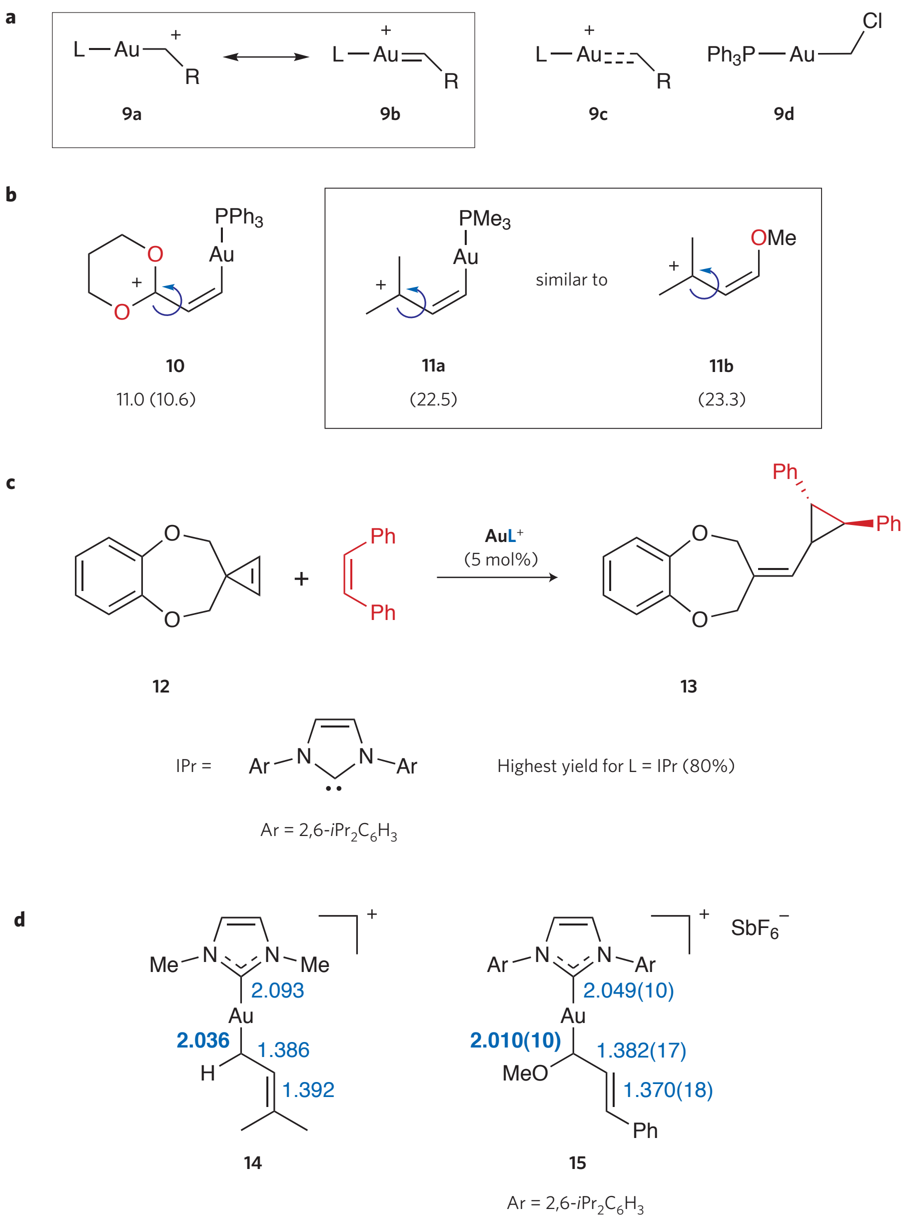

Figure 2 | Determining the nature of bonding in homogeneous gold catalysts. **a**, Cationic or carbene structures for [L–Au(I) –CHR]$^+$. **b**, Experimental and calculated (in parenthesis) bond-rotation energies for allyl carbocations (kcal mol^{-1}). **c**, Gold-catalysed cyclopropanation of *cis*-stilbene with **12** via gold carbenes of type **9b**. **d**, Calculated and experimental (X-ray diffraction) bond distances (Å), respectively, for cation **14** and complex **15** (ref. 12); standard deviations are given in parentheses.

It is also common practice to depict extreme cases such as the highly strained 1-norbornene (**5**), 1,2-cyclohexadiene (**6**), cyclopentyne (**7**) and benzyne (**8**) (Fig. 1c) as members of the alkene, allene and alkyne classes of compounds despite their highly distorted structures[2].

Therefore, it is hardly surprising to come across arguments in the field of organometallic chemistry where metals with *d* orbitals are involved and bonding acquires a higher level of sophistication. The relatively young field of homogeneous gold catalysis has not been an exception. Now on page 482 of this issue, Toste and colleagues address[3] the nature of the gold–carbon bond in [L–Au(I)–CHR]$^+$ complexes, an issue that has led recently to certain levels of controversy[4,5]. These intermediates have been interpreted by different authors as gold-stabilized carbocations **9a** or gold carbenes **9b** (Fig. 2a), and are the key players in gold(I)-catalysed activations of alkynes — a type of transformation that leads stereoselectively to complex structures under very mild conditions[6,7]. As a note of caution on the use of the term metal carbenoid as synonym of metal carbene, it may be important to mention that a genuine gold carbenoid, Au(PPh$_3$)(CH$_2$Cl) (**9d**), is a stable complex that has been structurally characterized[8].

Recently, the group of Alois Fürstner reported that gold cations — such as **10** — have rotational barriers around the C2–C3 bond that are more consistent with an open carbocationic structure[5] (Fig. 2b). *Ab initio* calculations performed by Toste and co-workers support this view. However, analysis of allylic system **11a**, which does not have strongly carbocation-stabilizing oxygen atoms, shows that the Au–PMe$_3$ fragment has a donating effect that is comparable to a methoxy group — a well known carbocation-stabilizing group — or the two methyl groups of a tertiary cationic centre.

The length of the gold–carbon bond was calculated to be highly dependent on the ligand attached to gold. Thus, in complexes of type **11a**, the shortest bond (1.97 Å) was found for the π-donating chloride ligand, whereas phosphite or phosphine complexes have longer bonds (2.04–2.06 Å). Interestingly, intermediates with N-heterocyclic carbene (NHC) ligands, which are strongly σ-donating and very weakly π-acidic, show relatively short Au–CR$_2$ bonds, more consistent with the carbene rendition **9b** of Fig. 2a. This is confirmed experimentally by Toste and colleagues in the cyclopropanation of an alkene, a reaction that is characteristic of metal carbenes[9,10] (Fig. 2c). Thus, in gold-catalysed reaction of cyclopropene **12**, the highest yield of adduct **13** was realized with a gold catalyst bearing IPr, an NHC ligand, which leads to a more carbene-like gold intermediate. The influence of ligands on the structures of the key intermediates in gold-catalysed cyclizations of 1,6-enynes has also been noted[11].

It is also instructive to compare the calculated bond distances for cation **14** with those determined by X-ray diffraction for complex **15** (ref. 12), which shows a carbon–gold bond with the allylic ligand shorter than that calculated by Toste and co-workers for **14** (Fig. 2d). The C1 carbon resonance of **15** appears at 281.5 ppm in the ^{13}C NMR spectrum, which is consistent with a gold-carbene formulation.

Despite the nature of these reactive species as gold carbenes (**9b**), the overall gold–carbon bond order is around 1, which corresponds to partial σ and π bonds. Although structure **9a** shows a bond of order 1 between gold and carbon, this misleading representation suggests that a simple σ bond is involved. The more precise representation **9c** (Fig. 2a) is more cumbersome and it is not likely that it would be adopted by the chemical community. A similar situation was discovered previously for rhodium carbenes (often named carbenoids) $L_nRh{=}CR_2$, where the formulation of a 'double half-bond' model was first proposed[13]. Despite the apparently unorthodox concept of double half-bonds, which might lead to raised eyebrows, weak carbon–metal double bonds are more common than many recognize. For example, very low rotational barriers around the $Ru{=}CR_2$ bond — only a few kcal mol^{-1} — have been found in Grubbs carbenes, widely used as catalysts in olefin metathesis[14].

In issues of this type some could be tempted to paraphrase Gertrude Stein saying that "a bond is a bond is a bond", however, recognizing the subtleness of chemical bonding and the importance of ligand-tuning is essential for achieving the desired reactivity in organometallic catalysis as has been so well illustrated in the research of Toste and co-workers. Citing Tantillo and Hoffmann[15]: "As beautiful and useful as chemistry is, nothing chemical is likely to be simple." ❐

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ORGANIC SYNTHESIS

New uses for old building blocks

New methodology that couples together carbonyl compounds with boronic acids shows much promise for synthesis owing to ease of access of the building blocks, functional group tolerance and broad scope of the reaction.

Varinder K. Aggarwal

In much the same way that a child with a number of different types of Lego pieces can make a vast array of complex structures (Fig. 1a), an organic chemist can create amazingly complex compounds from a relatively small number of simple molecular building blocks. However, that is where the analogy between building Lego models and organic synthesis ends. Although it may take a child just a few hours to create an elaborate model, it is likely to take many man-years to construct a complex molecule — piecing together organic building blocks is not as easy as piecing together Lego.

In general, the two ends of the molecular building blocks have to be activated in some way to make them 'sticky' before they can be joined together. Furthermore, the activation process has to be selective for a specific site, which becomes increasingly difficult for increasingly complex molecules. Thus, methods that combine readily available building blocks under mild conditions are very important to the continued

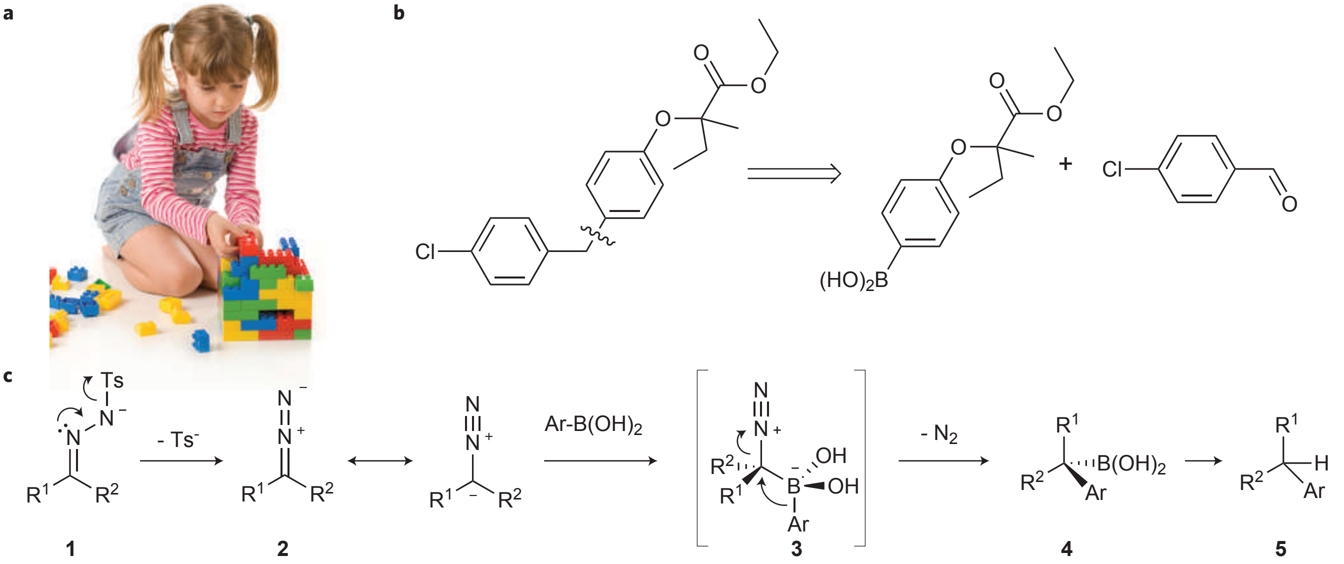

Figure 1 | Construction of complex chemical compounds from simple building blocks. **a**, The oft-used analogy between building molecules and building Lego models only goes so far. **b**, The pharmaceutical beclobrate (Becloscerin). A potential disconnection that is made possible by the newly described methodology is indicated. **c**, Proposed mechanism of the reaction of hydrazone salt **1** with a boronic acid. Ts, *p*-toluenesulfonyl; Ar, Aryl.