

It is actually quite straightforward to use self-assembly at the liquid–solid interface to form a 2D lattice (monolayer) of molecule-based nanowells. A pioneering example of a one-molecule-thick, nanoporous, self-assembled network at a solid–liquid interface is based on hydrogen-bonding interactions between trimesic acid (TMA, 1,3,5-benzenetricarboxylic acid) building blocks⁴. As a result of the planar structure of the molecule and the symmetrical positioning of the trigonal exodentate functional groups, in most cases porous networks form through equivalent hydrogen-bonding interactions between carboxylic acid groups. TPTC, having four carboxylic acid groups, is also a perfect building block for forming a monolayer of regularly spaced nanowells at the liquid–solid interface³, but it is different. Because of the position of the carboxylic acid groups, two hydrogen-bonded dimer motifs are possible: the two terphenyl groups in a dimer can run parallel or make an angle of 60°. Through the fortuitous match between the length of a terphenyl group and the length of two hydrogen-bonded benzoic acid moieties, a regular lattice is formed by a random combination of both dimer motifs. As a result, there are five non-equivalent types of hexagonal pores that are similar though not identical in size (~1 nm).

Self-assembled structures with a regular lattice of nanowells of about 1 nm in diameter can trap guest species such as coronene within the monolayer, as demonstrated for

trimesic acid³. Now Beton, Champness and colleagues achieve a similar feat with the addition of C₆₀ to the TPTC network. The beauty and novelty of their results, however, is in the formation of a surface-based bilayer structure caused by the addition of the guest molecule. On adding C₆₀, they witnessed — using scanning tunnelling microscopy — the formation of a second nanoporous layer of TPTC, in contrast to experiments on C₆₀ and TMA during which only monolayer formation with C₆₀ guest adsorption was observed⁵. Neither C₆₀ adsorption nor the growth of the second layer of TPTC was observed in isolation, indicating a co-dependence of these processes. The C₆₀ molecule prefers to adsorb in a specific one of the five types of pore in the initial layer, one in which three terphenyl groups make up three of the edges of a hexagon, as this type has the smallest internal size and highest binding energy. The relative orientation of the TPTC molecules in the second layer, however, seems not to be affected by the initial layer. Islands of TPTC/C₆₀ nucleate at separate sites and grow into small disconnected domains.

Interestingly, on addition of the flat and disk-shaped molecule coronene, the bilayer/C₆₀ structure is destroyed: a single-layer TPTC network is formed with coronene immobilized within its pores. In contrast to C₆₀, coronene is preferentially adsorbed in pores where the hydrogen-bonded motifs, rather than the terphenyl groups, form the edges of the hexagonal pore.

Beton, Champness and colleagues have succeeded in realizing a 3D architecture through a transition from a 2D pattern by adding an appropriate guest molecule. The results are important because, although it is not difficult to form highly regular monolayers at the liquid–solid interface, the formation of well-defined multilayer structures is not trivial at all, especially if one cannot rely on donor–acceptor interactions⁶. Indeed, in the TPTC/C₆₀ system discussed here, the second layer could be removed on demand by scanning the STM tip, leaving the first layer unaffected. Moreover, laying the foundations for a strategy to form well-defined multilayer networks, as in this new research, is an important step in creating surface-supported functional 3D supramolecular materials. □

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CARBENES AND ALKYLIDENES

Spot the difference

Transition-metal carbenes and alkylidenes are sometimes considered similar species with subtly different bonding and reactivities. Investigations into scandium and yttrium carbenes have raised questions about our understanding — and definition — of these widely used compounds.

Daniel J. Mindiola and Jennifer Scott

Transition-metal carbenes and alkylidenes (ironically considered interchangeable by some) have remarkable functionalities and are widely used in group transfer and polymerization catalysis involving the formation of C–C bonds¹. Fundamentally, these ligand types differ in the electronic structures of the M=C bond (Fig. 1a) and, hence, also in their reactivities. Setting ground rules for reactivity and electronic properties between carbenes and alkylidenes is, of course, a formalism in that it raises a distinction between these two classes of ligand. Why then does a metal carbene sometimes react like an alkylidene and vice versa?

Taking advantage of the highly electropositive nature of rare-earth metals, two independent papers in the *Journal of the American Chemical Society* by teams led by Stephen Liddle² and the late Pascal Le Floch and Nicholas Mézailles³ show that a carbene-type ligand can also engage in alkylidene-like reactivity by virtue of tweaking the electronics of the ligand or metal centre in question. These two contributions highlight the increasingly blurred division between transition-metal carbenes and alkylidenes and raise questions regarding our strict definitions separating the two.

Transition-metal carbenes, often called Fischer carbenes after their discoverer⁴, consist of a M=CR₂ unit where the carbene fragment is viewed as a singlet species engaged in σ -donation to the metal centre and having an empty *p* orbital ready to accommodate π -donation from both the metal and the π -donor substituents (where R represents a π donor in Fig. 1a) coordinated to the carbene α -carbon⁵. Transition-metal carbenes are often generated with electron-rich metal centres and the carbene ligand is often considered electrophilic owing to the vacant *p* orbital on the α -carbon. Originally reported by Schrock⁶, and shortly thereafter

by Tebbe and co-workers⁷, alkylidenes are sometimes referred to as Schrock carbenes and conversely have a triplet ground-state electronic structure, forming M=C bonds with early transition metals through the radical recombination of two triplet fragments, M and CR₂ (ref. 5; Fig. 1a). The R substituents are generally alkyls or alkyl-like groups, consequently resulting in the formation of a highly polarized M=C bond with a nucleophilic carbon centre reminiscent of Wittig-type reagents, R₃P⁺-C-R₂.

Despite the rigorous classifications described above, exceptions certainly exist. For example, there are amphiphilic M=C units that react in both Fischer- and Schrock-like manners⁸, and there are

also examples in which a partial negative charge on the α-carbon does not imply a nucleophilic moiety⁵. Conceivably, the best set of guidelines to distinguish each M=C type should be judged by a combination of analysis of the M=C bond and, perhaps more convincingly, its mode of reactivity.

The chemistry reported by the groups of Liddle² and Le Floch³ similarly involve the reactivity of two variations of a tethered carbene, M=C, either in the form of a doubly deprotonated *bis*-sulfidophosphorane or *bis*-iminophosphorane ligand, both of which are prototypical of Fischer carbenes. Paradoxically, they seem to react (to some extent) like Lewis-acid-stabilized (Tebbe-like)⁷ and Schrock-like⁶ alkylidenes,

a result that narrows even further the subtle differences between Fischer and Schrock carbenes.

In the work of Le Floch, Mézailles and colleagues³, the scandium carbene complex ([S=PPh₂]₂C)ScCl(py)₂ (**1**) reacts with benzophenone to form the corresponding olefin, [S=PPh₂]₂C=CPh₂ (**3**), and an intractable material presumed to be 'ScOCl' (Fig. 1b). Although the intermediate scandium oxo, **A**, was not isolated from the latter reaction, another oxo-intermediate, namely the scandium tetramer **2** (having a Sc₄O₂ core and depicted in Fig. 1b), was obtained by using a depleted amount of ketone (0.5 equiv.). The scandium oxo tetramer is probably formed by means of a metallo-Wittig-like reaction of the carbene ligand **1** with O=CPh₂, and is best represented as a combination of two ([S=PPh₂]₂C)ScCl(THF)₂ molecules with two hypothetical 'ScOCl' fragments.

Alkylidene-like behaviour of an yttrium carbene was reported separately by Liddle and co-workers², but with a twist. Reaction of the complex ([Me₃SiN=PPh₂]₂C)Y(OR)(THF) (**4**; R = C(CH₂SiMe₃)₂Ph₂) with benzophenone did not result in group transfer of the carbene ligand to the CPh₂ unit of the ketone. Rather, *ortho* C-H bond activation by the carbene takes place to generate a hypothetical carbanion (or other resonant forms for transient **B**; Fig. 1c). The carbanion further inserts another equivalent of O=CPh₂ to form intermediate **C**, and finally cyclizes to form the corresponding *isobenzofuran* (Fig. 1c). Isotopic labelling studies suggest the C-H bond-breaking to be the rate-determining step for the overall reaction. As a consequence of the rate-limiting regioselective C-H bond activation of benzophenone by the carbene ligand, further steps follow rapidly, such as C-C and C-O bond-forming reactions, to ultimately form the coordinated heterocycle in **5**.

Using this convergent approach to the activation of additional substituted ketones, the group² elegantly demonstrate the ability of **4** to convert an enolizable ketone, such as O=C(Me)Ph, to a more complex organic product, such as dypnopinacol, following hydrolysis of the reaction mixture³. This new approach seems promising for the stoichiometric preparation of heterocycles with stereocentres that would otherwise be difficult to prepare by more laborious, multistep syntheses.

In alkylidene reagents stabilized by Lewis acids (Tebbe- or Schrock-type), enolizable protons are often overlooked owing to the decreased basicity of the alkylidene carbon relative to prototypical phospho-Wittig-like reagents⁷. Although the reactivity of complex **1** with enolizable ketones is unknown³,

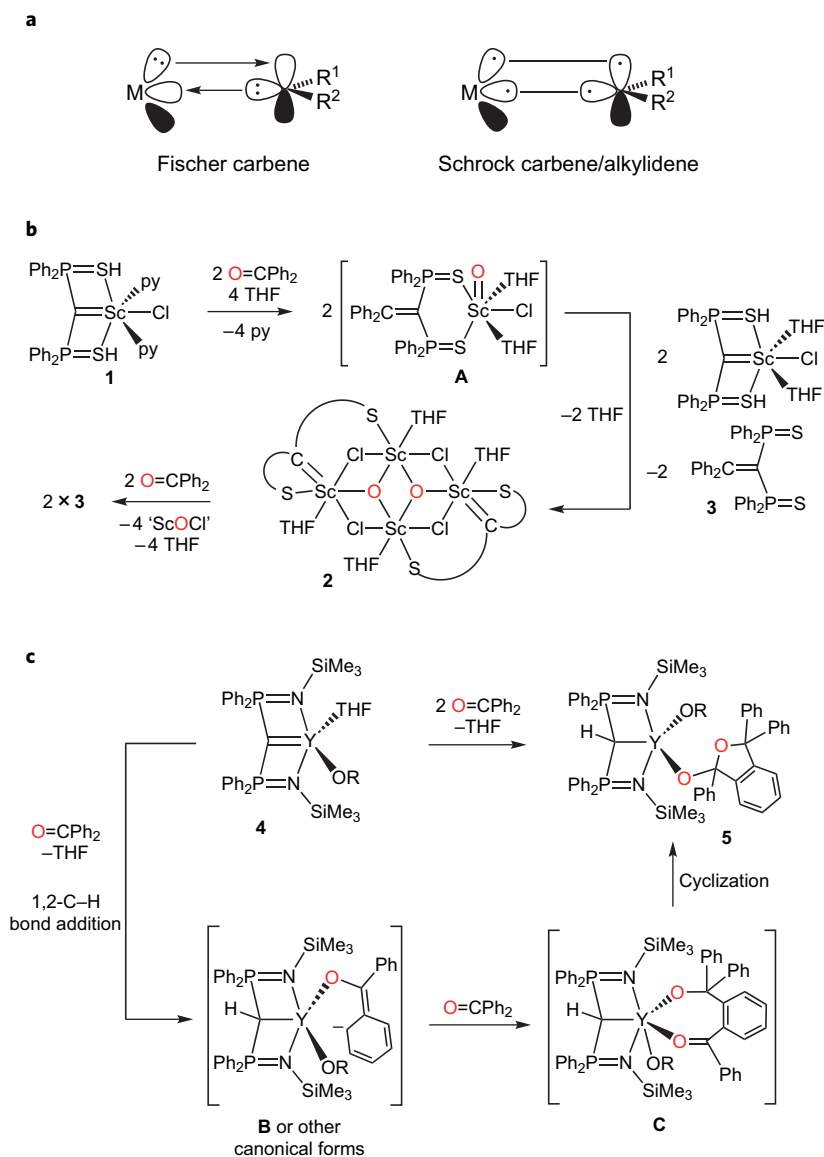


Figure 1 | Comparison of the reactivities of scandium and yttrium carbenes. **a**, Bonding differences between carbenes and alkylidenes. **b**, Wittig-like reactivity of the scandium carbene complex **1** ultimately to form **3** by means of intermediates **A** and **2**. **c**, C-H bond activation, insertion and cyclization reaction with the aid of the yttrium carbene **4**. Me, methyl; Ph, phenyl; py, pyridine, THF, tetrahydrofuran.

its close analogue **2** seems basic enough to promote C–H bond activation of the enolizable proton over the aryl C–H bond². Apparently, the diagonal relationship between phosphorus and carbon may render groups such as $\sim\text{P}(\text{X})\text{Ph}_2$ (X = S or NSiMe₃) far more alkyl-like than would be anticipated, thereby making the α -carbon more nucleophilic than a classical Fischer carbene. This contrast in reactivity observed for the carbene framework $[\text{X}=\text{PPh}_2]_2\text{C}^{2-}$ demonstrates our limited perception of the differences between carbenes and alkylidenes.

Only time will tell whether terminal alkylidene complexes of the rare-earth metals can be isolated or even generated^{9,10}, and how their reactivities will differ from those of Fischer and Schrock carbenes or their alkali-metal counterparts. Very recent studies by Chen and colleagues¹¹ have established that a rare-earth metal can be no different from a transition metal because they isolated a stable, terminal scandium imide, in the form of (L)Sc=NAr(DMAP) (L = CH₃C(2,6-ⁱPr₂-C₆H₃N)CHC(CH₃)NCH₂CH₂NMe₂, Ar = 2,6-ⁱPr₂C₆H₃, DMAP = 4-dimethylamino pyridine). The complex is remarkably robust and

was fully characterized, in particular by single-crystal crystallography¹¹. The fact that a rare-earth imide complex can be isolated using the right choice of ancillary ligands (monoanionic and hard tridentate ligands in combination with a good neutral donor such as DMAP) hints that it is just a matter of time before the neighbouring carbon or oxygen analogues can be strategically prepared.

It would also be interesting to assess how a compound such as $([\text{X}=\text{PPh}_2]_2\text{C})\text{Li}_2$ or a hypothetical species such as $([\text{X}=\text{PPh}_2]_2\text{C})\text{M}$ (M = Ca or Mg) reacts with O=CPh₂. Are we on the verge of discovering a new type of transition-metal carbene ligand that extends beyond the nucleophilic scale of superbases such as Schlosser's reagent¹² (KCH₂R, where R is an alkyl group)? Given the awkward geometry of these carbene ligands (which are in fact almost T-shaped at carbon), a more in-depth orbital and bonding analysis is certainly warranted. □

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Correction

In the version of the Editorial 'Stop press' originally published (*Nature Chem.* **2**, 791; 2010), the name of Leibniz was mis-spelled. This has now been corrected in the HTML and PDF versions: 16 November 2010.