

Their model showed that the saturated concentration of small molecules on terraces, even at infinitely long times is negligible and that only large molecules could accumulate in significant enough numbers to produce the sort of surface coverage observed in the experiments. They calculated that the shortest molecules with sufficiently high terrace concentration to initiate formation of self-assembled domains are approximately 15 carbon atoms in length, very close to what was visualized in the STM images.

These STM observations and the modelling offer new insights into Fischer–Tropsch synthesis. Induction periods are often seen for this process, but they have often been explained through the initial formation of an active catalytic phase. The results of Navarro and colleagues suggest another explanation; the induction period is the time during which the monolayer of hydrocarbon molecules is formed and this monolayer endows beneficial effects on the catalytic system. When the terraces of the catalyst are nearly fully covered with domains of product molecules, the catalyst surface is

still catalysing the synthesis of more products molecules; as mentioned earlier the catalysis is performed at step sites and they are still available (Fig. 1b). The consequence of the formation of such an assembled layer is to bring about a change in the interaction between the product molecules and the catalyst surface. After this incubation period, the terrace surface is covered with product molecules; new product molecules cannot access the cobalt surface directly and can only interact with the molecular overlayer. The interaction between the newly formed product molecules and the overlayer of product molecules is quite weak and thus this weak interaction accelerates the desorption of the new product molecules.

Since its conception<sup>3</sup>, STM has been one of the most useful techniques available for studying model-catalyst surfaces under vacuum. In the past two decades, various instrumentation developments of STM have led to their intergration into reaction cells for *in situ* studies<sup>4–9</sup>. The work of Navarro and colleagues now clearly demonstrates the unique ability of STM in visualizing

adsorbates on a single-crystal model catalyst during catalysis. However, challenges still remain, for example, studying the surface of a high-surface-area catalyst under even higher pressures and temperatures. These targets, and further insights into the mechanisms of catalytic reactions, can be met through a concerted collaboration between chemists, materials scientists and microscope manufacturers. □

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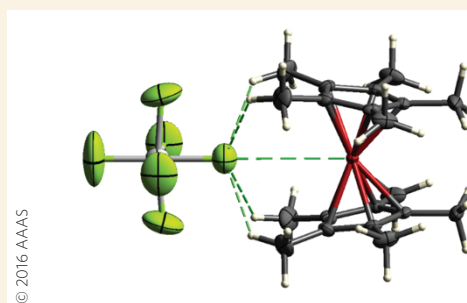
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## ORGANOMETALLIC CHEMISTRY

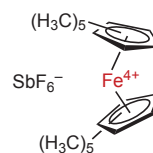
# Taking ferrocenium up a notch

Few organometallic compounds are as well known as ferrocene; it was one of the first compounds identified as having metal–carbon bonds and inspired decades of work studying metallocenes. It has a rich history in chemical catalysis and medicinal chemistry in the +2 oxidation state, where its stability and simple derivatization have proven to be beneficial, but although most stable in this state, it is also often encountered as the ferrocenium cation in its +3 oxidation state. Simple complexes of iron in its +4 oxidation state are, however, quite scarce, typically limited to fleetingly stable species (for example  $\text{Fe}_4^{4+}$ ) or those with metal–ligand multiple bonds. Early work in the area suggested that the permethylated derivative of ferrocene could be oxidized twice, but efforts to isolate the dicationic product were regularly met with defeat, implying that the  $\text{Fe(IV)}$  analogue of ferrocene would not be stable enough to characterize.

Now, a team led by Moritz Malischewski at the Free University Berlin and Karsten Meyer at Friedrich-Alexander University have successfully prepared — and isolated — various salts of the decamethylferrocene dication



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Decamethylferrocene(IV) dication

through oxidation of decamethylferrocene with  $\text{AsF}_5$ ,  $\text{SbF}_5$  and  $\text{ReF}_6$  in liquid  $\text{SO}_2$  (*Science* **353**, 678–682; 2016). These extraordinarily powerful oxidants proceed to convert the orange, 18-electron  $\text{Fe(II)}$  complex to the brown, 16-electron  $\text{Fe(IV)}$  complex in a stepwise fashion. Malischewski, Meyer and colleagues confirmed the oxidation- and spin-states of the products with magnetic susceptibility measurements and Mössbauer spectroscopy; both were consistent with a  $\text{Fe(IV)}$  complex, with  $S = 1$ .

In contrast to previous efforts to prepare the decamethylferrocene dication using transition-metal oxidants, the salts prepared in this work are stable at room temperature under an inert atmosphere. Whereas the

$\text{Fe(II)}$  and  $\text{Fe(III)}$  complexes have linear structures, the decamethylferrocene dication is bent along the  $\text{Cp}^*-\text{Fe}-\text{Cp}^*$  axis, the extent of this depending on the size of the counteranion. These unusual structures can be explained using the ‘polarizable ion model’, which accounts for similar effects in decamethyltitanocenium complexes. Although applications of such  $\text{Fe(IV)}$  complexes are unclear at present, even isolating these rare organometallic complexes was little more than a pipe dream even a few years ago, underscoring the importance of fundamental inorganic synthesis in modern chemistry.

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