

ORGANOMETALLIC CHEMISTRY

High-valent iron gets homoleptic



Only then will we know whether this exceptional complex is just a curiosity or an entry into a wider and basically uncharted territory of organometallic chemistry and catalysis



The diverse roles that iron has in natural and laboratory environments require it to assume a range of oxidation states — each a guise with a distinct personality. In the +IV state, iron can strip hydrogen from C–H bonds, allowing the installation of a halogen or an oxygenic group. Although such base-metal-catalysed direct functionalizations are attractive and intensely studied, our understanding of Fe(IV) complexes that are often proposed as intermediates has yet to catch up. Homoleptic species are particularly elusive, which increases the significance of the [Fe(alkyl)₄] complexes — prepared by disproportionation reactions — reported in *Angewandte Chemie International Edition* by a team led by Alois Fürstner.

Taming a strong Lewis acid such as Fe(IV) typically calls for anionic ligands that are both σ - and

π -basic. Despite this, FeF₄ — a D_{2d} -symmetric molecule — only persists within a noble gas matrix. The distorted square-planar ketimido complex [Fe(Bu₂CN)₄] and salts of [Fe(C₅Me₅)₂]²⁺ are more robust, although interactions with counterions contribute to the stability of the latter. Alkyl ligands are strong σ -bases, but their lack of π -basicity makes [Fe(alkyl)₄] species, with their low formal Fe valence electron count, all the more striking. The first such complex to be isolated was [Fe(1-norbornyl)₄], in which the bulky norbornyls crowd the Fe(IV) centre in a tetrahedral geometry. The carbocyclic ligands interdigitate so as to minimize steric strain that might otherwise render the complex unviable. The bulky organic groups participate in London dispersion interactions that, along with the four Fe–C bonds, hold the complex together.

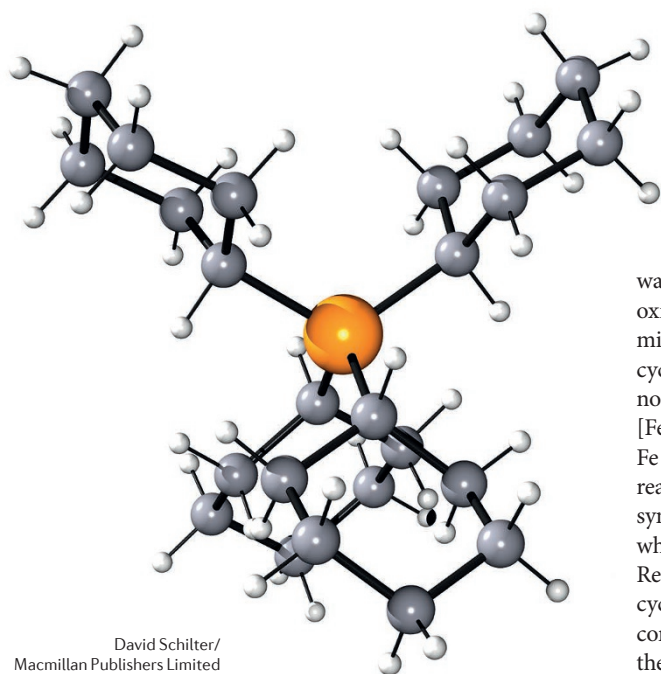
While studying C–C coupling reactions, Fürstner and colleagues considered the reduction of iron catalysts with Grignard reagents.

In some cases, Fe(II) or Fe(III) precursors afforded high-valent iron complexes among their products. This is a strange phenomenon: “it was totally unexpected to isolate an oxidized complex from a reaction mixture comprising FeCl₂ and cyclohexylmagnesium chloride,” notes Fürstner. The team found that [Fe(cyclohexyl)₄] forms alongside Fe metal in a disproportionation reaction that was also used in the synthesis of [Fe(1-norbornyl)₄], of which they were unaware at the time. Reflective of the strong donicity of cyclohexyls, the new tetrahedral complex is low-spin ($e^4t_2^0$) because the ligands give rise to a large ligand

field splitting ($\Delta_1 = 40 \text{ kcal mol}^{-1}$). Cyclohexyls are smaller than norbornyls, so the reasonable stability of [Fe(cyclohexyl)₄] at –20°C is interesting given its more exposed Fe(IV) centre and attenuated dispersion interactions. Such interactions appear to tip the Fe(II or III)–Grignard system in favour of disproportionation: [Fe(2-adamantyl)₄] could be prepared, but examples with ligands smaller than cyclohexyl could not.

Although similar in nature, [Fe(cyclohexyl)₄] differs from [Fe(1-norbornyl)₄] in that the former features Fe bound to C atoms that each bear a H atom. It is remarkable that an electrophilic centre such as Fe(IV) does not participate in significant agostic interactions with the C–H groups (let alone abstract an α - or β -hydride), an observation ascribed to these being situated just outside the lobes of the three d orbitals in the t_2 set. It remains conceivable that [Fe(cyclohexyl)₄] could bind suitably small substrate molecules using these vacant orbitals. Higher levels of theory are required to understand the metastability of [Fe(cyclohexyl)₄], which is tentatively rationalized by Fürstner in terms of stereoelectronics and dispersion forces. “Only then,” he adds, “will we know whether this exceptional complex is just a curiosity or an entry into a wider and basically uncharted territory of organometallic chemistry and catalysis.”

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ORIGINAL ARTICLE Casitas, A. *et al.* Two exceptional homoleptic iron(IV) tetraalkyl complexes. *Angew. Chem. Int. Ed.* <http://dx.doi.org/10.1002/anie.201612299> (2017)

FURTHER READING Liptrot, D. A. & Power, P. P. London dispersion forces in sterically crowded inorganic and organometallic molecules. *Nat. Rev. Chem.* **1**, 0004 (2017)