# Chapter 1

Selective oxygenations of hydrocarbons are important reactions. Owing to the fact that dioxygen is a triplet and therefore will not react readily with singlet molecules, activation is required, often involving free radicals or metal ions. For practical reasons, one would like to stop the oxidation process at an intermediate stage, like an alcohol or epoxide. An attractive reaction model is one in which a metal ion could split dioxygen producing a metal oxo species that could oxygenate a substrate. A mechanism of this type is the so-called oxo-rebound, which was first proposed by Groves.[1,2] To drive the first half of the reaction (dioxygen cleavage) the metal oxo bond has to be strong, but the second half requires a weak bond. The question has remained open whether both half reactions can run smoothly employing a single metal complex.

In looking at different metals, it is important to keep in mind periodic trends. Metal-oxo bonds tend to weaken as one moves up and to the right of the transition metal series. The first row is a classic example. Titanium and vanadium tend to form very strong bonds with oxygen, to such an extent that V(III) is used as an oxygen abstraction reagent, turning NO-metal species into nitrido compounds. [3] Moving to the right yields progressively more reactive species, with Fe and Mn oxos being the most reactive, whose oxo compounds have to be generated with an oxidant and are generally too unstable to be isolated. Iron is of course the most biologically relevant metal due to its presence in enzymes such as P-450 where an oxo metal species is presumed to be part of the cycle.

Moving past iron is problematic due to what is known as the oxo wall. Previous work in this group in particular focused on the use of perhalogenated porphyrins[4-6] and vanadium salen compounds[7] as catalysts. While catalytic activity was observed, it was not due to oxo transfer chemistry. Rather, the reactions proceed via the well-known peroxo-radical mechanism.[8] In both cases, it was apparent that oxo chemistry did not happen, owing either to a too reactive or a too stable metal oxo species. Of the remaining metals in the first row, only Cr forms oxo compounds that are more stable than those of Fe.

Cr-oxo porphyrins were first reported by Groves.[9,10] Of the two oxo oxidation states (V and IV), complexes in the former are too reactive to be isolated, while ones in the latter are stable and can be spontaneously formed from the corresponding chromium(II) species.[11] The first isolable Cr(V)O species was reported by Kochi using a salen ligand.[12] However, the increased stability of the compound was still not high enough to observe a spontaneous oxidation of the Cr(III) species. In the literature, prior to our work, there was only one reported example of a stable Cr(V) oxo complex, that of Collins' tetraamido ligand.[13]

Related to porphyrins, corroles have been known since the 1960s.[14] Among their most promising properties is their ability to stabilize high oxidation states. The native corrole is too insoluble to be of any synthetic use. As in the case of porphyrins, bulky meso groups need to be added to improve solubility. Unfortunately, there was no route available to such compounds until the early 1990s.[15] The first corroles to be synthesized were solubilized via alkyl chains in the β-positions. While that solved solubility problems, it severely limited the ability to tune the ligand framework.

From previous research, it is known that the degree of halogenation of the porphyrin framework greatly affects the reactivity of the compound, to such an extent that there is a good correlation between the redox potential of the metal and higher activity. Since corroles stabilize high oxidation states better than porphyrins, it is expected that some of their complexes might be too inert for useful oxygen atom transfer chemistry. Halogenation of the corrole framework could bring their reactivities into a useful range, however.

The main challenge is to find a synthetic route to those compounds. As mentioned above, the most studied corrole ligands all have substitution at the β position, making it difficult to tune ligand properties. Also, the absence of meso aryl groups make those ligands extremely vulnerable to oxidative degradation. While the meso-aryl problem was partially solved in the early 1990s, substitution at the β position remained necessary, not for solubility reasons, but for synthetic reasons, this time.[15]

While various schemes are available for the synthesis of the corrole framework, most of these are complex multistep routes, which make them of little use in large scale production of the ligand. In fact, the limited availability of the ligand is in part to blame for the sparse information available on the chromium complex. Only three papers have been published on chromium corroles to date, none really giving more information than the previous one, and all of them revealing little about the chemistry of this compound.

It was only in 1999 with the breakthrough synthesis of Gross et al.[16] that it became possible to produce corroles on a large scale (50 mg/day). After that, we decided to embark on a study of its chromium complexes, mainly because we felt that this metal had the most promise of yielding an oxo-transfer catalyst.

The first step was to metalate the complex and figure out what oxidation state is spontaneously formed. Even though corroles stabilize high oxidation states, the presence of pentafluorophenyl groups in the meso position of the ligand tend to reverse this trend. Starting with $Cr(CO)_6$, we obtained a Cr(V)O corrole, which is an astounding 5-unit change in oxidation state upon metallation. Work on this complex is reported in Chapter 2.

We then proceeded to make Cr complexes in other oxidation states. From porphyrin studies, it is known that chromium porphyrins can exist in various oxidation states, from Cr(V) to Cr(II). Using various methods, we managed to isolate compounds in oxidation states ranging from one-electron oxidized Cr(V)O down to Cr(III). The results are reported in Chapter 3.

Having isolated all the complexes, we then studied their reactivities, as described in Chapter 4. We found that Cr(III) reoxidizes in air to the Cr(V)O state, but that this compound can only oxidize phosphines.

We then halogenated the ligand. In Chapter 5, we report studies on the gallium complex, which serves as a model for ligand bromination.

Finally, in Chapter 6, we report a chromium octabromocorrole and its reactivity. While the Cr(V)O state is reactive enough to oxidize styrenes, the Cr(III) state reoxidizes very slowly in air. In an effort to increase the reactivity of the Cr(III) state, we removed the axial pyridine ligands via acid trapping. This yielded a complex that was able to oxidize styrenes in air catalytically.

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