

## Preface

# Organometallic chemistry with N and O $\pi$ -donor ligands

There is a large body of main group, transition and *f*-element metal chemistry based around N and O  $\pi$ -donor ligand complexes, much of which can be traced back to the pioneering works of Bradley, Chatt, Lappert, Wannagat and others. The chemistry of N and O  $\pi$ -donor ligands spans the classic boundaries of 'organometallic' and 'coordination' compounds, as will be apparent from the contributions herein.

The chemistry of organometallic compounds containing N-donor (e.g. amide, imide) and O-donor (e.g. alkoxide, oxide)  $\pi$ -ligands has been a continuing growth area, particularly since the mid-1980s; it forms the main focus of this Special Issue. These anionic ligands can act as potent  $\pi$ -donors to transition and actinide metals, and tend to stabilise metals in medium to high oxidation states, and those with otherwise low valence-electron counts. In this regard and in others, they differ fundamentally from the neutral,  $\pi$ -acceptor ligands such as carbonyl, arene, alkene and phosphine, the chemistry of which is more typically associated with comparatively lower oxidation states and filled valence shells. The  $\pi$ -donor nature of the N and O  $\pi$ -ligands also leads to their typical occurrence (which derives from the oxidation state and low valence-electron count preferences) with early to middle transition metals.

Several characteristic features of these N and O  $\pi$ -donor ligands combine to make them interesting and

versatile ligands in both fundamental and applied organometallic chemistry. (i) For imide, amide and alkoxide ligands there is considerable scope for controlling steric, electronic and solubility characteristics by suitable modification of the N- and O-bound organic substituents; (ii) the  $\pi$ -donor ability of the ligands (and hence the number of electrons formally donated to a metal centre) can be relatively flexible, responding to the number and  $\pi$ -properties of other ligands present and the geometry at the metal centre, as well as being modulated by the formal hybridisation at the N or O atoms (e.g. 'linear' or 'bent' imides or alkoxides); (iii) from the point of view of compound synthesis there are a wide range of reliable protocols now available for introducing N and O  $\pi$ -donor ligands; (iv) in the case of imide and oxide compounds in particular, it is important to recognise the two very different facets of these groups, namely their ability to act either as spectator (or ancillary) ligands or as reactive sites, thereby directly engaging in new bond-forming and bond-breaking reactions.

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