Review

Redox-coupled structural changes in copper chemistry: Implications for atom transfer catalysis

Timothy J. Zerk, Paul V. Bernhardt *

School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane 4072, Australia

A R T I C L E   I N F O

A B S T R A C T

The coordination chemistry of copper is dominated by its monovalent and divalent oxidation states and interplay between the two is central to the role of copper-based homogeneous catalysts. Upon reduction of most copper(II) complexes, which commonly are five coordinate, the coordination number rapidly changes to four or less. This feature is advantageous for atom transfer reactions where single electron transfer is coupled to the association or dissociation of a radical. Although this coupled change in coordination number and oxidation state is central to the mechanism of atom transfer reactions, its importance to catalysis is not widely appreciated. Herein we review the structural chemistry of copper(I) and copper(II) with a range of multidentate N-donor ligands employed in atom transfer radical polymerisation (ATRP). The remarkable resistance of copper(I) to accept more than four donor atoms is illustrated and discussed in the context of both its solid state and solution structures.

© 2017 Elsevier B.V. All rights reserved.

Contents

1. Introduction

The chemistry of copper complexes is dominated by the divalent oxidation state due to their typically greater stability in air and in aqueous solution compared with monovalent analogues. However, various discrete, monomeric complexes of copper(I) have recently been deployed as the reagents of choice (catalytic or stoichiometric) for effecting several powerful and versatile synthetic transformations which are of considerable interest in both academic and industrial settings (Scheme 1). Thus the advent of

* Corresponding author.
    E-mail address: p.bernhardt@uq.edu.au (P.V. Bernhardt).
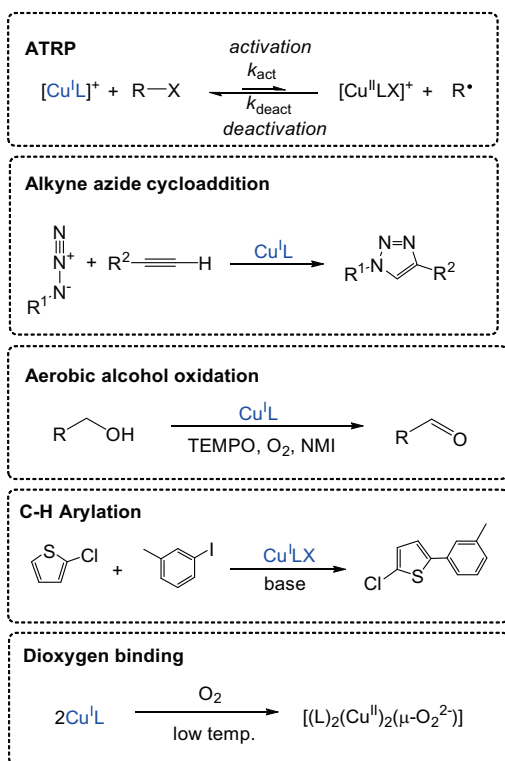
Scheme 1. Key synthetic reactions involving Cu^{I}L complexes. In ATRP and heterocycle arylation 'X' is a halogen. NMI is N-methylimidazole. Charge is omitted for clarity in most cases and solvent co-ligands are not included.

copper-based (i) atom transfer radical polymerisation (ATRP) [1], (ii) alkyne azide cycloaddition ('click') chemistry [2–4], (iii) aerobic alcohol oxidations [5,6] and (iv) C—H arylation reactions [7,8] coupled with a persistent interest in model complexes for non-haeme-containing di-oxygen transporters [9–12] and monooxygenase enzymes [13] has led to an active interest in the chemistry of cuprous compounds.

The most common ligands for these cuprous reagents are multidentate N-donors, which stabilize copper in both the +2 and +1 oxidation states; a number of these are collected in Chart 1. Symbolising the chelating ligand as 'L', the corresponding copper(I) complexes may be described by the general notation $[Cu^I(L)_a(X)_b]^n$ where X is a monodentate co-ligand and n is the overall charge. Changing the identity of the ligand 'L' (and/ or additional co-ligand/s) has a significant effect on the reaction kinetics, selectivity or control in each of the Cu-based reactions listed above.

One point of interest concerning these cuprous complexes is their coordination number. Many of the Cu^I reagents which are used in the reactions shown in Scheme 1 are described as '5-coordinate' complexes and a significant number of these have been structurally characterised. However, careful inspection of the solid-state structures reveals that most of these contain a distortion within the first coordination sphere. Through this distortion, one or more of the donor atoms partially, or completely, dissociates from the metal centre so the true coordination number is less than five. Various types of distortion are observed as will be discussed, yet the overall effect in each case is to lower the formal coordination number usually to four. In this contribution we review the structures of copper(I) complexes bearing the ligands shown in Chart 1 and explore the prevalence of this distortion and also its implications for reactivity.

1.1. Cu-catalysed atom transfer radical polymerisation

In particular this discussion will be framed within the context of Cu-based ATRP. This continues to be an important area of research both in stand-alone synthesis of functionalized polymers, and in combination with other synthetic transformations such as alkyne azide cycloaddition chemistry, or other controlled polymerisation methods. A Chemical Abstracts Service search[1] revealed almost 21,000 journal articles relating to ATRP since its inception in 1995. Catalysts containing various transition metal ions have been used in ATRP including those of groups 5 (V) [14], 6 (Mo) [15,16], 7 (Mn) [17], 8 (Fe and Ru) [18–24], 9 (Co) [25,26] and 10 (Ni) [27,28], but the vast majority of studies utilise Cu [29–35] (Fig. 1) and that is our focus here.

In classical ATRP the catalyst ($[Cu^IL]^+$) reacts with a dormant radical precursor (RX, X = Br or Cl); a halogen-terminated alkyl chain. Inner sphere halogen atom transfer to copper(I) releases an alkyl radical (R·) and produces the higher oxidation state, halido–metal complex ($[Cu^{II}(L)X]^+$) through homolytic scission of the R—X bond [36,37]. This reaction is coined 'activation' (Scheme 1) and is characterised by the rate constant k_{act}. The key point is that during activation the coordination number *and* the oxidation state of the Cu ion must increase by one. The reverse reaction, deactivation, quenches the radical and regenerates the catalyst. Thus, throughout an ATRP synthesis, the Cu catalyst is constantly oscillating between the +2 and +1 oxidation states and at the same time is changing coordination number. In this regard it is essential to understand the structure of a given copper(I) catalyst and how it relates to the structure of its corresponding copper(II) partner.

An additional aspect which requires some comment is the relation between the structures in the solid state and solution; the phase in which these complexes find their natural application. Where possible, solid state and solution structural characterisation will be compared and contrasted. The most logical division of the compounds is by the denticity of the N-donor ligand and the remainder of the review is organised as such.[2] An additional feature apparent in Chart 1 is that all of the ligands bear either heterocyclic or tertiary amine N-donors. This predominance of N-donor ligands lacking NH groups in complex with copper(I) has persisted in the ATRP field since inception.

2. Ligand classes

2.1. Structural classification

Before proceeding it is worth outlining the parameters which will be used to define the coordination geometry of the complexes discussed herein. The ubiquitous τ_5-parameter introduced by Addison et al. will be used to describe the distortion of 5-coordinate transition metal complexes. The terms α and β refer to the largest and second largest coordinate angles so τ_5 varies from ideal square pyramidal ($\tau_5 = 0$) to trigonal bipyramidal ($\tau_5 = 1$) geometry [38] (Eq. (1a) and Scheme 2).

The corresponding, τ_4 function developed by Houser and co-workers [39] will be used to classify the coordination geometry of 4-coordinate complexes. The value of τ_4 is calculated by applying Eq. (1b) where α and β are again the two largest coordinate angles (Scheme 2). At one extreme $\alpha = \beta = 109.5°$ ($\tau_4 = 1$) and the complex is tetrahedral while at the other extreme $\alpha = \beta = 180°$