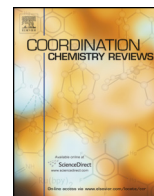




Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Metal compounds of boron-substituted alkoxide ('boroxide') ligands

Martyn P. Coles*

School of Chemical and Physical Sciences, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand

Contents

1. Introduction and background.....	00
1.1. Note on nomenclature	00
1.2. Motivation for research	00
2. Synthetic approaches	00
3. Spectroscopic and structural aspects.....	00
4. Review of compounds	00
4.1. Main group metal compounds.....	00
4.1.1. Group 1 metals	00
4.1.2. Group 2 metals	00
4.1.3. Group 13 metals.....	00
4.2. Transition metal compounds.....	00
4.2.1. Group 3 metals	00
4.2.2. Group 4 metals	00
4.2.3. Group 6 metals	00
4.2.4. Group 7–9 metals.....	00
4.2.5. Group 12 metals.....	00
5. Summary and future developments.....	00
References	00

ARTICLE INFO

Article history:

Received 26 January 2016
Received in revised form 9 March 2016
Accepted 9 March 2016
Available online xxx

Keywords:

Boron-alkoxide
Boroxide
Borinic acid
Metal complex

ABSTRACT

The inclusion of boron atoms into traditional oxygen-based alkoxide ligands has been implemented to alter the steric and electronic components of the metal–oxygen bond. This class of ligand, colloquially termed 'boroxide', has been examined as a method to influence the reactivity at the metal centre, with an emphasis on catalytic reactions. This review summarizes the work in this area.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction and background

Alkoxide ligands, $[\text{RO}]^-$ are an integral part of inorganic and coordination chemistry that have been studied since early research efforts in these disciplines [1]. The ability to tune ligand properties by varying the R-group has led to the application of this ligand class

in many branches of the chemical sciences, including catalysis and as pre-cursors to materials. Each alkoxide ligand is capable of acting as a $[1\sigma, 2\pi]$ donor group able to contribute up to 6 electrons to a metal centre. One approach that has been used to moderate the donor ability of this general ligand type is the incorporation of a boron-containing group (which is able to accept electron density) adjacent to the oxygen. This review summarizes the work in one of the areas in which this approach has been applied, specifically the $[\text{R}_2\text{BO}]^-$ ('boroxide') anion, focussing on the use of these species as a ligand in coordination chemistry.

* Tel.: +64 04 463 6357.
E-mail address: martyn.coles@vuw.ac.nz

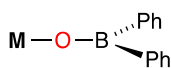


Fig. 1. The diphenylboroxide ligand bonded to a generic metal centre, **M** (R groups arbitrarily chosen to illustrate the nomenclature adopted in this review).

1.1. Note on nomenclature

The parent (neutral) compounds from which the ligand class featured in this review are derived are borinic acids, with general formula R_2BOH . The anion formed from deprotonation of the hydroxyl functionality, $[R_2BO]^-$, has acquired a number of different names in the literature, including the disubstituted 'borinato-', 'boroxo-', 'boroxy-', 'boranyloxy-' and 'boroxido-' ligand. According to IUPAC nomenclature, a more accurate general description for $[R_2BO]^-$ is the disubstituted 'oxidoborate(1-)-' ligand, where additional descriptors using the *kappa* convention would need to be included to make it clear which groups are attached to boron.

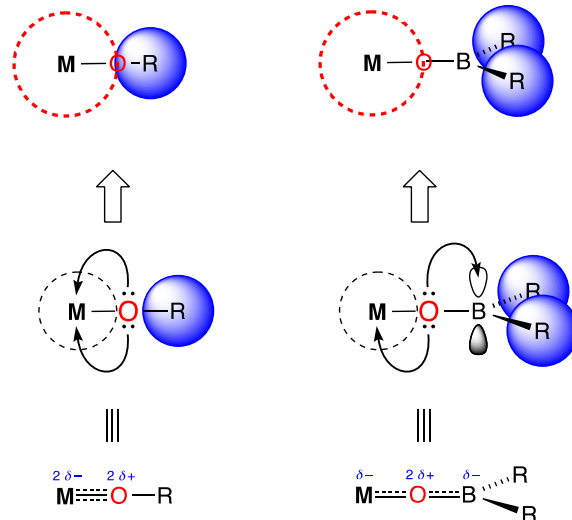
In this review article, we adopt the most commonly used term for the $[R_2BO]^-$ anion in the context of coordination chemistry, namely the boroxide ligand. This naming relates the ligand to the corresponding alkoxide, $[RO]^-$, and siloxide, $[R_3SiO]^-$, ligands. Unless otherwise stated and in accordance with most common coordination mode (see Section 3), the generic boroxide ligand in this review assumes a η^1 -coordination through the oxygen atom. Thus the diphenylboroxide ligand refers to the $[Ph_2BO]^-$ ligand coordinated to a single metal **M** through the oxygen atom (Fig. 1).

1.2. Motivation for research

In addition to tuning the steric profile of a ligand class, the ability to manipulate the extent to which the group donates/accepts electron density to a metal centre is key to the development of productive chemistry. Much of the work pertaining to boroxides has focussed on the concept that they will behave as 'electron-deficient' alkoxide ligands due to the presence of an empty acceptor orbital on the boron atom. In conventional alkoxide chemistry, the lone-pairs on oxygen are available to donate to suitable orbitals on the metal fragment. As such this ligand class plays a predominant role in the coordination chemistry of electron deficient metal centres (e.g. early transition metal elements, lanthanides) and is much less common in the chemistry of the late *d*-block metals. With the boroxide ligand, however, the *O*-atom lone pairs are of the correct symmetry to be able to combine with the empty *2p*-orbital on the boron atom, resulting in less electron density available for donation to the metal centre. The net result is that the boroxide behaves as a poor electron-donor compared with an alkoxide, and the metal can therefore be considered electron-deficient when compared with a structurally similar alkoxide complex. This is illustrated schematically in Fig. 2, showing the extreme cases in which both of the oxygen lone-pairs are delocalized, consistent with the linear geometry of the oxygen atom that is most commonly found in both ligand classes.

An additional consequence of incorporating the boron atom in this ligand system is a shift of the (typically bulky) *R*-groups from the immediate coordination sphere of the metal (Fig. 2). Therefore whilst the boroxide ligand contains twice as many *R*-substituents as an alkoxide, the presence of an additional 'spacer' atom displaces this bulk away from the metal. A positive aspect of this is that the boroxide ligand enables better access to the metal centre, which may be a positive attribute in the design of catalytically active species.

Sterically:
- less demanding



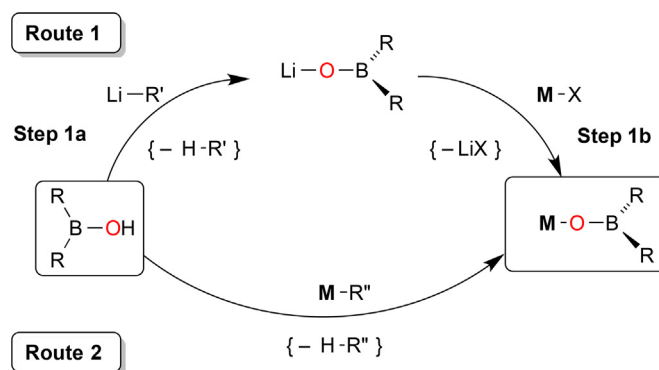
Electronically:
- relatively 'electron poor'

Fig. 2. Schematic of the potential for boroxide ligands to act as electron deficient analogues of alkoxide ligands.

2. Synthetic approaches

The most common synthetic method for installing a boroxide ligand at a metal centre is through a salt-metathesis approach (Route 1, Scheme 1). For bulky boroxide ligands (e.g. *R* = mes) the first step of Route 1 involves generation of a group 1 metal salt. This route most commonly proceeds via lithium boroxide compounds (Step 1a), which are conveniently prepared from the reaction with commercially available organolithium reagents (e.g. *n*-BuLi, MeLi) with the corresponding neutral borinic acid. Subsequent reaction of the lithium boroxide with a metal halide (Step 1b) proceeds with elimination of LiX (*X* = halogen) and transfer of the boroxide to the metal **M**. Although the lithium salts can be isolated (see Section 4.1.1) the reactions are most often conducted with the 'LiOR₂' reagent generated *in situ*. It should be noted that this route is not favoured for less sterically hindered boroxides, where a competing pathway is present in which the alkyllithium reagent attacks the electrophilic boron atom.

An alternative route that has been used to synthesize boroxide compounds involves protonolysis of a suitable organometallic (or metal-amido) precursor by the parent borinic acid, leading to the



Scheme 1. General strategies for the synthesis of metal boroxides. Route 1: salt metathesis; Route 2: protonolysis.

Download English Version:

<https://daneshyari.com/en/article/5150950>

Download Persian Version:

<https://daneshyari.com/article/5150950>

[Daneshyari.com](https://daneshyari.com)