University of Groningen

Redox-behavior and reactivity of formazanate ligands

Mondol, Ranajit

DOI:
[10.33612/diss.107969043](https://doi.org/10.33612/diss.107969043)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2019

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Mondol, R. (2019). *Redox-behavior and reactivity of formazanate ligands: Boron and aluminum chemistry*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen.
<https://doi.org/10.33612/diss.107969043>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Redox-behavior and reactivity of formazanate ligands

Boron and Aluminum Chemistry

Ranajit Mondol

The research described in this thesis was carried out at the Stratingh Institute for Chemistry, University of Groningen, The Netherlands.

The work was financially supported by the Netherlands Organization for Scientific Research (NWO)

Cover designed by Ranajit Mondol
Printed by Ipskamp Printing, The Netherlands

ISBN (printed version): 978-94-034-2154-4
ISBN (electronic version): 978-94-034-2153-7

university of
 groningen

Redox-behavior and reactivity of formazanate ligands

Boron and Aluminum Chemistry

PhD thesis

to obtain the degree of PhD at the
University of Groningen
on the authority of the
Rector Magnificus Prof. C. Wijmenga
and in accordance with
the decision by the College of Deans.

This thesis will be defended in public on

Friday 20 December 2019 at 11.00 hours

by

Ranajit Mondol

born on 9 March 1991
in Nischintapur, West Bengal, India

Supervisor

Prof. E. Otten

Prof. W.R. Browne

Assessment Committee

Prof. J.G. Roelfes

Prof. S. R. Harutyunyan

Prof. M. Driess

Dedicated to my beloved mother (maa) and wife...

Table of Contents

Chapter 1	1
Introduction	1
1.1 General introduction	2
1.2 Redox-active ligands	2
1.2.1 Utilization of redox-active ligands by Nature	3
1.2.2 Bio-inspired and artificial redox-active ligands	4
1.2.2.1 Terminal alkene hydrosilylation catalyzed by iron complexes containing redox-active ligands	5
1.2.2.2 Redox reactions in main group complexes	6
1.3 Formazanate ligands	9
1.3.1 General features of formazans	9
1.3.2 Redox-active properties of formazanate ligands	11
1.4 Overview of the thesis	14
1.5 References	16
 Chapter 2	 23
Stable, crystalline boron complexes with mono-, di- and trianionic formazanate ligands	23
2.1 Introduction	24
2.2 Synthesis and characterization of boron compounds bearing formazanate ligands in their monoanionic form	24
2.3 Synthesis and characterization of boron compounds bearing formazanate ligands in their di- and trianionic forms	25
2.3.1 Synthesis of 1- and 2-electron reduced products	25
2.3.2 Analysis of X-ray crystallographic data of 1- and 2-electron reduced products	26
2.3.3 Analysis of EPR spectroscopic data of 1-electron reduced products	27
2.3.4 Characterization of 2-electron reduced products by NMR spectroscopy	28
2.3.5 UV-Vis spectroscopy of neutral, 1- and 2-electron reduced formazanate boron compounds	29

2.4 Computational studies	29
2.5 Conclusions	30
2.6 Experimental section	31
2.6.1 General considerations	31
2.6.2 Compounds synthesis and characterization	32
2.6.3 X-ray crystallography.....	35
2.7 Supplementary information.....	38
2.7.1 UV-Vis spectra.....	38
2.7.2 Determination of exchange kinetics in compound 4b.....	38
2.7.3 Computational studies.....	41
2.8 References	444

Chapter 3..... 47

Reactivity of 2-electron reduced formazanate boron compounds with electrophiles:

Facile N-H/N-C bond homolysis due to formation of stable ligand radicals 47

3.1 Introduction	48
3.2 Reactivity of 2-electron reduced formazanate boron diphenyl compound with electrophiles	51
3.2.1 Ligand-centered storage of 2-electron and electrophile ($2e^-/E^+$) in formazanate boron diphenyl compound.....	51
3.2.2 Investigation of hydrogen evolution from H_3^-	53
3.2.3 Exploration of N-H and N-C bonds cleavage in H_3^- and Bn_3^-	54
3.2.3.1 Investigation of N-H bond cleavage in H_3^- by 2D EXSY NMR spectroscopy	54
3.2.3.2 Investigation of N-H bond Cleavage in H_3^- by following the kinetics of H-atom transfer to TEMPO.....	55
3.2.3.3 Investigation of N-C(Bn) bond cleavage in Bn_3^- by following the kinetics of benzyl transfer to TEMPO	55
3.3 Conclusions	56
3.4 Experimental section	58
3.4.1 General considerations	58
3.4.2 Compounds synthesis and characterization	58

3.5 Supplementary information.....	60
3.5.1 EPR spectral data	60
3.5.2 UV-Vis spectral data.....	61
3.5.3 2D EXSY NMR studies	61
3.5.4 Analysis of reaction kinetics $^{(F)Bn}3^-$ + TEMPO	63
3.6 References	69

Chapter 4..... 73

Aluminum complexes with redox-active formazanate ligand: Synthesis, characterization, and reduction chemistry 73

4.1 Introduction	74
4.2 Synthesis and characterization of formazanate aluminum complexes.....	76
4.2.1 Synthesis and characterization of bis(formazanate) aluminum complex.....	76
4.2.2 Synthesis and characterization of mono(formazanate) aluminum complexes.....	78
4.2.2.1 Synthesis and characterization of mono(formazanate) aluminum dialkyl and (monoiodo) (monoalkyl) complexes.....	78
4.2.2.2 Synthesis and characterization of mono(formazanate) aluminum diphenyl and diiodide complexes	79
4.3 Analysis of UV/Vis spectroscopic data of formazanate aluminum complexes	82
4.4 Reduction chemistry of formazanate aluminum complexes	84
4.4.1 Reduction chemistry of bis(formazanate) aluminum complex	84
4.4.2 Reduction chemistry of mono(formazanate) aluminum complexes	85
4.4.2.1 Reduction chemistry of mono(formazanate) aluminum diphenyl complex ..	85
4.4.2.2 Reduction chemistry of mono(formazanate) aluminum diiodide complex ...	86
4.5 Conclusions	88
4.6 Experimental section	89
4.6.1 General considerations	89
4.6.2 Compounds synthesis and characterization	90
4.6.3 X-ray crystallography.....	94
4.6.4 Computational studies.....	95

4.7 Supplementary information.....	96
4.7.1 Cyclic voltammetry.....	96
4.7.2 EPR spectroscopy.....	98
4.7.3 UV/Vis spectroscopy.....	98
4.7.4 Computational data.....	99
4.8 References.....	100

Chapter 5..... 103

Structure and bonding in reduced boron and aluminium complexes with formazanate ligands..... 103

5.1 Introduction.....	104
5.2 The hindered rotation around the N-C(Ph) bonds in two-electron reduced formazanate aluminium diphenyl compound (2^{2-}).....	105
5.3 Reactivity study of two-electron reduced formazanate aluminium diphenyl compound (2^{2-}) with benzyl bromide.....	107
5.3.1 Synthesis of ligand-benzylated product $Bn2^-$, and its characterization by NMR spectroscopy.....	107
5.3.2 Crystallographic characterization data of ligand-benzylated products $Bn1^-$ and $Bn2^-$	108
5.3.3 The evaluation of ligand-benzylated products $Bn1^-$ and $Bn2^-$ by DFT calculations.....	110
5.3.4 Characterization of ligand-benzylated product $Bn2^-$ by UV/Vis spectroscopy.....	111
5.4 Investigation of the cleavage of the N-C(Bn) bond in $Bn2^-$	112
5.5 Conclusions.....	113
5.6 Notes.....	114
5.7 Experimental section.....	114
5.7.1 General considerations.....	114
5.7.2 Compounds synthesis and characterization.....	115
5.7.3 X-ray crystallography.....	117
5.7.4 Computational studies.....	119
5.8 Supplementary information.....	120

5.8.1 UV-Vis spectroscopy	120
5.8.2 NMR spectra	120
5.8.3 Estimation of upper limit of the barrier for N-C(Ph) bond rotation in 1 ²⁻	121
5.8.4 Determination of exchange kinetics in compound 2 ²⁻	121
5.8.5 Analysis of reaction kinetics of [B ¹][NBu ₄] + TEMPO, [B ²][Na] + TEMPO and [B ²][NBu ₄] + TEMPO.....	123
5.8.6 Computational and X-ray crystallographic characterization data	127
5.9 References	129

Chapter 6..... 133

Cation effects on dynamics of ligand-benzylated formazanate boron and aluminium complexes 133

6.1 Introduction	134
6.2 Investigation of nitrogen inversion in ligand-benzylated formazanate boron and aluminium complexes	135
6.2.1 Investigation of nitrogen inversion in [B ¹][Na] and [B ¹][NBu ₄]	135
6.2.2 Investigation of nitrogen inversion in [B ²][Na] and [B ²][NBu ₄]	139
6.2.3 Exploration of alkali-metal cations effects on the dynamic process.....	140
6.3 Conclusions	142
6.4 Experimental section	143
6.4.1 General considerations	143
6.4.2 Compounds synthesis and characterization	143
6.5 Supplementary information.....	146
6.5.1 UV/vis spectroscopy	146
6.5.2 Determination of activation parameters for the dynamic process in compounds [B ¹][Na], [B ¹][K], [B ¹][Rb], [B ¹][NBu ₄], [B ²][Na] and [B ²][NBu ₄].....	146
6.6 References	155

Chapter 7	159
Mechanism of H-abstraction from ligand-protonated formazanate boron complex: a computational study	159
7.1 Introduction	160
7.2 Mechanistic details of net H-atom transfer from $^{\text{H}}\text{I}^-$ to TEMPO by intrinsic bond orbital (IBO) method	162
7.2.1 Computational details.....	162
7.2.2 Intrinsic bond orbital (IBO) analysis to elucidate the mechanism of net H-atom transfer from $^{\text{H}}\text{I}^-$ to TEMPO	162
7.3 Conclusions.	166
7.4 References	168
 English Summary	 171
Nederlandse Samenvatting	177
Acknowledgements	183
List of Publications	189