Open-shell nitrene- and carbene-complexes of cobalt
Characterisation and reactivity
Goswami, M.

Publication date
2017

Document Version
Other version

License
Other

Citation for published version (APA):

General rights
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), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Open shell nitrene– and carbene-complexes of cobalt: characterisation and reactivity

Monalisha Goswami
Open-shell nitrene- and carbene-complexes of cobalt: characterisation and reactivity

ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Universiteit van Amsterdam
op gezag van de Rector Magnificus
prof. dr. ir. K. I. J. Maex
ten overstaan van een door het College voor Promoties
ingestelde commissie,
in het openbaar te verdedigen in de Aula der Universiteit
op vrijdag 10 november 2017, te 11:00 uur

door

Monalisha Goswami
Geboren te Tirap, India
Promotiecommissie

Promotores: Prof. Dr. B. de Bruin (Universiteit van Amsterdam)

Prof. Dr. J. N. H. Reek (Universiteit van Amsterdam)

Overige Leden: Prof. Dr. M. P. Doyle (University of Texas at San Antonio)

Prof. Dr. J. H. van Maarseveen (Universiteit van Amsterdam)

Prof. Dr. S. Woutersen (Universiteit van Amsterdam)

Prof. Dr. C. J. Elsevier (Universiteit van Amsterdam)

Dr. E. Gallo (Università degli Studi di Milano)

Dr. Ir. J. I. van der Vlugt (Universiteit van Amsterdam)

Faculteit: Faculteit der Natuurwetenschappen, Wiskunde en Informatica

The research presented in this dissertation was performed at the Homogeneous, Supramolecular and Bio-inspired Catalysis group at the van ’t Hoff Institute for Molecular Sciences of the University of Amsterdam. The work was financially supported by the Netherlands Organization for Scientific Research through an NWO-CW VICI Grant (project 016.122.613) to B. de Bruin.
Nothing in life is to be feared, it is only to be understood. Now is the time to understand more, so that we may fear less.

Marie Skłodowska-Curie

You cannot hope to build a better world without improving the individuals. To that end, each of us must work for his own improvement and, at the same time, share a general responsibility for all humanity, our particular duty being to aid those to whom we think we can be most useful.

Marie Skłodowska-Curie
The cover, designed by the author is her impression (acrylic on paper) of the colourful molecules, called porphyrins; a macrocycle that has been profusely used in this thesis as a ligand. Their presence can give colours to the wings of certain butterflies and their lack is what strips the green to give way to the autumn colours, let's say, in the Norwegian woods.
~ For my parents Nivedita and Ashok and my sister Manisha ~
# Table of Contents

**Chapter 1**
Introduction: Substrate non-innocence and open-shell organometallic reactivity.  

**Chapter 2**
Characterisation of porphyrin-cobalt(III)-‘nitrene radical’ species relevant in catalytic nitrene-transfer reactions.  

**Chapter 3**
Geometry and spectroscopic metal oxidation state of mono- and bis-nitrene radical complexes based on the cobalt-porphyrin platform; An X-ray Absorption Spectroscopy (XAS) study.  

**Chapter 4**
Porphyrin-Co(III)-‘nitrene radical’ catalysed synthesis of phenoxazinone and o-amino-azobenzenes.  

**Chapter 5**
Synthesis, characterisation and application of anionic [Co(II)(Cor)]⁻ corrole complexes in ring-closing C – H amination of an aliphatic azide.  

**Chapter 6**
Cobalt(II) porphyrin catalysed synthesis of indolines via a 1,5-H atom transfer pathway.  

**Chapter 7**
Difluorocarbene (CF2) transfer from a cobalt complex to an electron-deficient alkene.  

**Summary**  

**Samenvatting**  

**List of Publications**  

**Acknowledgements**