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Publication date

2018

Document Version

Final published version

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Citation for published version (APA):

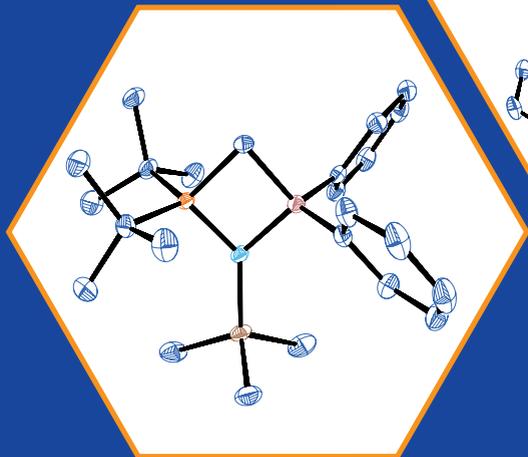
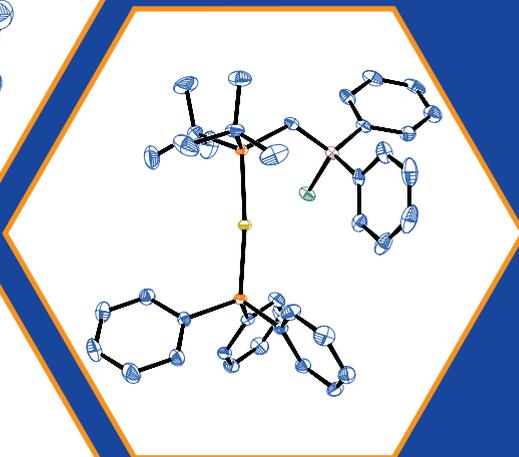
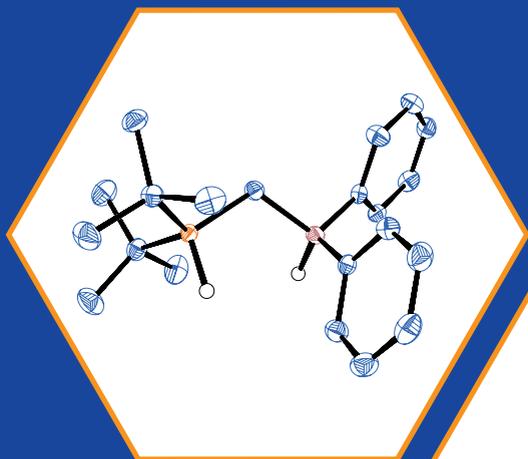
Boom, D. H. A. (2018). *From activation to stabilization: Different applications of a frustrated Lewis pair*. [Thesis, fully internal, Universiteit van Amsterdam].

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From
Activation
to
Stabilization

*Different Applications of a
Frustrated Lewis Pair*

Devin H. A. Boom

From Activation to Stabilization:
Different Applications of a Frustrated Lewis Pair

Devin H. A. Boom

2018

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The work described in this thesis was financially supported by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (NWO/CW, Grand No. 723.012.101).

Cover design by Chiara Derksen

Printed by ProefschriftMaken | www.proefschriftmaken.nl

ISBN: 978-94-6380-109-6

From Activation to Stabilization:
Different Applications of a Frustrated Lewis Pair

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 Agnietenkapel
op vrijdag 7 december 2018, te 14.00 uur

door

Devin Hendrik Arie Boom

geboren te Gouda

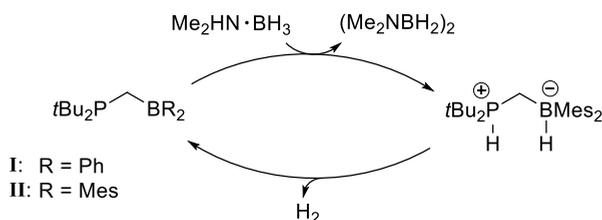
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Preface

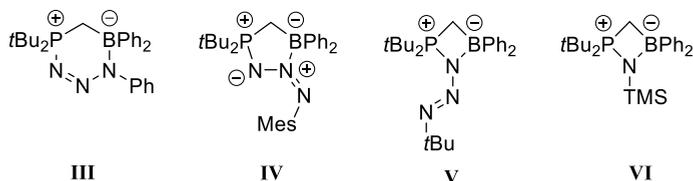
Since the discovery in 2006 that frustrated Lewis pairs (FLPs) can heterolytically split dihydrogen and subsequently can transfer the H^+/H^- pair to organic substrates, a new field of main-group chemistry and catalysis was born. Since then, FLPs have been applied in a broad range of different fields as they are reported to activate a large variety of small molecules, they can stabilize or trap highly reactive intermediates, and can also be utilized as ambiphilic, donor-accepter ligands in coordination chemistry and catalysis. In this thesis, we demonstrate the reactivity of geminal phosphorus/boron-based frustrated Lewis pairs in such a diverse field of chemistry.

As substrate in main-group chemistry, amine-boranes gained a lot of attention because of their potential as hydrogen storage materials. In **chapter 1** we provide a complete overview of the current state-of-the-art of all p-block based compounds that can facilitate the stoichiometric and catalytic dehydrogenation of amine-boranes. In addition, we found that our geminal P/B-based FLP **I** rapidly dehydrogenates dimethylamine-borane with concomitant formation of the corresponding H_2 -adduct. In **chapter 2** we highlight that a slight modification of the FLP, by using B-mesityl substituents (FLP **II**) instead of phenyl groups, results in catalytic turnovers.

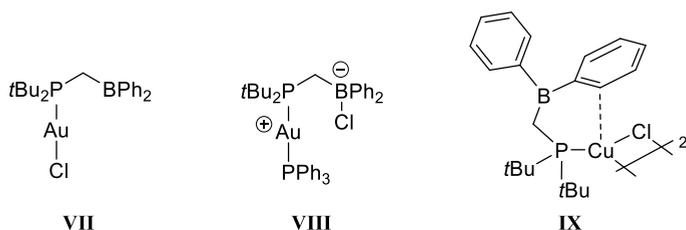


In **chapter 3** we demonstrate that FLP **I** can also stabilize the highly reactive “Staudinger-type” phosphazide intermediates in a fashion that is highly dependent on the azide substrate (**III–V**). Furthermore, the obtained nitrene-adduct **VI** retained its FLP-type

reactivity and by ring opening can capture small molecules, such as hydrogen chloride, tetramethylammonium fluoride and phenylisocyanate.



In **chapter 4** we illustrate the use of FLP **I** as ambiphilic ligand in gold(I) chemistry, and show that the coordination behavior of **I** is influenced by the gold(I) metal precursor. This results in displacement of a co-ligand (**VII**) versus heterolytic cleavage of the gold–chloride bond (**VIII**), and this distinct difference has been fully analyzed using DFT calculations. Additionally, **chapter 5** describes the reaction of FLP **I** with copper(I) chloride, which forms a dimeric copper(I) complex (**IX**) that exhibits green fluorescence when exposed to UV light.



The overarching component in chapter two to five is the development of FLPs, such as **I** or **II**, which are typically prepared via a salt metathesis reaction between an organolithium reagent, R_2PCH_2Li , and a diarylchloroborane, Ar_2BCl . In **chapter 6**, we introduce a novel methodology for the selective synthesis of a variety of diarylchloroboranes, utilizing a protection–deprotection strategy, which enables the straightforward preparation of these widely used boron building blocks that are now available for further research.