Vita

Candidate's name: Zachary Lucas Rees

Universities Attended:

University of New Brunswick (2020)
Bachelor of Science Honors

University of New Brunswick (2021)
Masters of Science

Turning Organic Reducing Agents Catalytic

UNIVERSITY OF NEW BRUNSWICK

THESIS DEFENCE AND EXAMINATION

in Partial Fulfillment

of the Requirement for the Degree of
Master of Science

by

Zachary L. Rees.

in the Department of Chemistry

U.N.B., Fredericton, N.B.

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via MS TEAMS

Examining Committee

Dr. C. Adam Dyker	Supervisor
Dr. Andreas Decken	Internal Examiner
Dr. Chris McFarlane	Int-Ext Examiner
Dr. Gilles Villemure	Chair of Oral Examination

Abstract

Bispyridinylidenes (BPYs) are a class of organic reducing agents (ORAs), which can be used to perform homogenous reductions under mild conditions that many classical reducing agents such as alkali metals cannot. Generally speaking, the molecular weights for BPYs far exceed those of the substrates, and most reductions employ an excess of BPY. This causes large scale reductions to be difficult, the overall cost of the reductions to be high, and difficulties during purification due to a large mass of BPY biproduct. In order to rectify these problems a two-component catalytic cycle was envisioned that involves sub-stoichiometric amounts of BPY as the active species for substrate reduction, and a sacrificial electron donor (SD) that continually regenerates the BPY from its oxidized form. A Cy_3PN-substituted BPY was chosen for this study based on its strong reduction potential, ease of preparation in both the reduced and oxidized forms, and it features phosphorus for easy monitoring of reactions by ^{31}P NMR spectroscopy. This BPY was used to reduce several phosphorous based substrates. Many sacrificial donors were tested however, only sodium appeared to be a viable option for the regeneration of the BPY from its oxidized form. The potential of this new two-component catalytic cycle is demonstrated through the successful reduction of dichlorotricyclohexylphosphorane (Cl_2PCy_3) producing tricyclohexylphosphine (PCy_3) using catalytic amounts (5-20 mol %) of the BPY along with an excess of sodium. Reductions were also attempted using only the sacrificial donor as a control which proved the necessity of the ORA.