



A study of stereochemical and electronic factors in the nickel promoted dimerization of norbornadiene [pt.I] : electro-organometallic catalysts [pt.II]
by Dale Grant Pillsbury

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
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Abstract:

To gain a better understanding of metal promoted cycloaddition reactions, the nickel promoted dimerization of norbornadiene (NBD) was examined from three aspects; stereochemical and electronic factors in the substrate and the influence of ligands bound to the nickel which are not directly involved in the reaction. As an example of stereochemical perturbation, the 7-methyl derivative of NBD was dimerized using bis(tri-phenylphosphine)dicarbonylnickel, $\text{Ni}(\text{CO})_2(\text{P}(\text{O})\text{C}_6\text{H}_5)_2$, as a promoter with both thermal and photochemical activation. It was found by an analysis of the nuclear magnetic resonance spectra of the dimers that both 2+2 and 2+2+2 cyclodimerization products were produced. The major dimers had the same skeletal stereochemical configurations as the dimers produced from the corresponding thermal and photochemical reactions of NBD and to investigate substrate electronic factors, norbornene, pentacyclotetradeca-5,11-diene (exo-trans-exo isomer) and [2,2,2]bicycloocta-2,5-diene were subjected, without success, to conditions found to produce dimers with NBD. A proposal describing the requisite electronic factors for active olefinic substrates was made. The influence of indirectly involved ligands was examined through a study of kinetics parameters in the thermal reaction of $\text{Ni}(\text{CO})_2(\text{P}(\text{O})\text{C}_6\text{H}_5)_2$ with NBD. The reaction was found to be very temperature sensitive, to be strongly inhibited by carbon monoxide and triphenylphosphine, and to exhibit an induction period followed by the major reaction period in which the rate of production of the two 2+2 dimers (both known) was constant. The kinetics results were viewed as the initial establishment of equilibrium between a number of competing reactions to produce very low steady state concentrations of active catalytic species. The substrate modification data and kinetics data were coordinated with the work of other investigators to give a unified picture of the nickel promoted cyclodimerization reaction.

The use of electrochemical regeneration of active organometallic coupling reagents was also studied. It was found benzyl halides, bromo-benzene, benzoyl chloride, phenacyl bromide and n-hexyl bromide could be coupled with electrochemically produced metal species. The reactions were run in single compartment cells using N,N-dimethylformamide as solvent, a catalytic amount of a metal ion and stabilizing ligands such as triphenylphosphine to prevent zero valent metal from plating out. Carbonyl insertion and a unique formylation reaction were also studied.

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PART I: A STUDY OF STEREOCHEMICAL AND ELECTRONIC FACTORS
IN THE NICKEL PROMOTED DIMERIZATION OF NORBORNADIENE

PART II: ELECTRO-ORGANOMETALLIC CATALYSTS

by

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PREFACE

At this point it would seem worthwhile to note that this thesis is divided into two separate parts. This has been done to maintain continuity and establish clarity. Thus, despite the fact that all the work reported here involves metal promoted organic reactions, it is felt the two parts differ sufficiently in intent and scope to merit this approach.

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ABSTRACT

To gain a better understanding of metal promoted cycloaddition reactions, the nickel promoted dimerization of norbornadiene (NBD) was examined from three aspects; stereochemical and electronic factors in the substrate and the influence of ligands bound to the nickel which are not directly involved in the reaction. As an example of stereochemical perturbation, the 7-methyl derivative of NBD was dimerized using bis(triphenylphosphine)dicarbonylnickel, $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$, as a promoter with both thermal and photochemical activation. It was found by an analysis of the nuclear magnetic resonance spectra of the dimers that both 2+2 and 2+2+2 cyclodimerization products were produced. The major dimers had the same skeletal stereochemical configurations as the dimers produced from the corresponding thermal and photochemical reactions of NBD and $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$. To investigate substrate electronic factors, norbornene, [8,2,1,14,7,2,02,9,03,8]pentacyclotetradeca-5,11-diene (exo-trans-exo isomer) and [2,2,2]bicycloocta-2,5-diene were subjected, without success, to conditions found to produce dimers with NBD. A proposal describing the requisite electronic factors for active olefinic substrates was made. The influence of indirectly involved ligands was examined through a study of kinetics parameters in the thermal reaction of $\text{Ni}(\text{CO})_2(\text{P}\phi_3)_2$ with NBD. The reaction was found to be very temperature sensitive, to be strongly inhibited by carbon monoxide and triphenylphosphine, and to exhibit an induction period followed by the major reaction period in which the rate of production of the two 2+2 dimers (both known) was constant. The kinetics results were viewed as the initial establishment of equilibrium between a number of competing reactions to produce very low steady state concentrations of active catalytic species. The substrate modification data and kinetics data were coordinated with the work of other investigators to give a unified picture of the nickel promoted cyclodimerization reaction.

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PART I

A STUDY OF STEREOCHEMICAL AND ELECTRONIC FACTORS IN THE
NICKEL PROMOTED DIMERIZATION OF NORBORNADIENE

INTRODUCTION

Toward an Understanding of Metal Promoted Cycloaddition

Among the various classes of organic reactions one may distinguish one group in which the construction of a ring occurs by the creation of two (or more) sides of that ring. The formation of these new sides occurs at the expense of unsaturation - frequently double or triple bonds - in the precursor addends. This class of organic reactions is known as cycloadditions. Thus, the formation of a cyclobutane ring from two molecules of ethylene would be the result of 2π electrons + 2π electrons (two double bonds) going to two single bonds, or in short, a 2+2 cycloaddition. The formation of cyclohexane (three new single bonds) from three molecules of ethylene would be one example of a 2+2+2 cycloaddition. The reaction of 1,3-butadiene (4π electrons) and ethylene (2π electrons) to form cyclohexene (two new single bonds and one new double bond) would be a 4+2 cycloaddition. In this case, the formation of two sides of a six member ring is attended by the creation of a new double bond as well.

Cycloaddition reactions may be divided into those which require only thermal or photochemical excitation and those in which a catalyst is used in conjunction with such excitation. The former group of cycloaddition reactions encompasses a large body of "classical" organic reactions with such notable examples as the Diels-Alder reaction, ozonization (a dipolar addition), the "ene" reaction, and the

photochemical cyclobutanation of olefins. It appears these reactions follow the conservation of orbital symmetry rules of Woodward and Hoffmann¹, if the reaction follows a concerted mechanism. In brief, the rules state that if there are an odd number of participating π electron pairs, the reaction will be thermally allowed, whereas, an even number of participating π electron pairs results in a photochemically allowed reaction.

Catalyzed cycloaddition reactions may be subdivided into general acid (or base) catalyzed cycloadditions, e.g. Lewis acid catalyzed Diels-Alder reactions, and metal catalyzed reactions. It is with a specific group of reactions in this latter class - cycloadditions catalyzed by transition metals in low oxidation states - that we shall be concerned here. These reactions hereafter shall be referred to as transition metal mediated (or promoted) cycloaddition reactions.

As implied above, in any cycloaddition reaction two alternative mechanistic pathways are conceivable; one concerted and the other non-concerted. Specifically, with regard to transition metal promoted reactions one may visualize a concerted cycloaddition occurring on a metal template in which all new bonds to form the product ring are formed simultaneously with no intermediates being present from reactants to products. One could also visualize a pathway involving the formation of intermediates incorporating the metal. This non-concerted reaction would lead to the product by elimination of the metal with ring closure.

