



Investigation of the dimerization of norbornadiene using photolysis of nickel and pseudo-nickel carbonyls  
by Gerald Elery Voecks

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

Dimers of norbornadiene are known to form when norbornadiene solutions of various metal carbonyls are thermally excited. Of the numerous stereoisomeric dimers which norbornadiene will form various mixtures of them are generated by different metal carbonyls. In order to obtain needed information regarding factors contributing to the path-way responsible for the stereospecificity of the dimers formed a series of isostructural and isoelectronic transition metal carbonyls—nickel and the pseudo-nickel carbonyl series—were investigated. In this series of compounds triphenylphosphine derivatives of the nickel, cobalt, and iron species were included. Photochemistry was used as the mode of excitation because of the ability to specifically excite the carbonyl complex independently of the norbornadiene. With the exception of nickel tetracarbonyl the series of compounds produced a specific dimer isomer—exo-trans-exo. Nickel tetracarbonyl produced two 2 + 2 + 2 or pseudo-Diels-Alder dimers of norbornadiene photochemically. Since this complex was unique in its dimer product formation and since it provided an opportunity to observe ligand participation by comparison to the bistrisphenyl-phosphinedicarbonylnickel complex the reaction was studied in detail. A norbornadiene complex as well as dimer complexes were isolated and their participation in the dimer formation process thermally and photochemically was studied resulting in a proposed mechanism for dimerization by nickel tetracarbonyl. The major 2+2+2 dimer also afforded the opportunity to study the effect of a cyclopropyl ring on neighboring protons in proton nmr experiments.

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## ABSTRACT

Dimers of norbornadiene are known to form when norbornadiene solutions of various metal carbonyls are thermally excited. Of the numerous stereoisomeric dimers which norbornadiene will form various mixtures of them are generated by different metal carbonyls. In order to obtain needed information regarding factors contributing to the pathway responsible for the stereospecificity of the dimers formed a series of isostructural and isoelectronic transition metal carbonyls—nickel and the pseudo-nickel carbonyl series—were investigated. In this series of compounds triphenylphosphine derivatives of the nickel, cobalt, and iron species were included. Photochemistry was used as the mode of excitation because of the ability to specifically excite the carbonyl complex independently of the norbornadiene. With the exception of nickel tetracarbonyl the series of compounds produced a specific dimer isomer—exo-trans-exo. Nickel tetracarbonyl produced two 2 + 2 + 2 or pseudo-Diels-Alder dimers of norbornadiene photochemically. Since this complex was unique in its dimer product formation and since it provided an opportunity to observe ligand participation by comparison to the bistrisphenylphosphinedicarbonylnickel complex the reaction was studied in detail. A norbornadiene complex as well as dimer complexes were isolated and their participation in the dimer formation process thermally and photochemically was studied resulting in a proposed mechanism for dimerization by nickel tetracarbonyl. The major 2 + 2 + 2 dimer also afforded the opportunity to study the effect of a cyclopropyl ring on neighboring protons in proton nmr experiments.

## INTRODUCTION

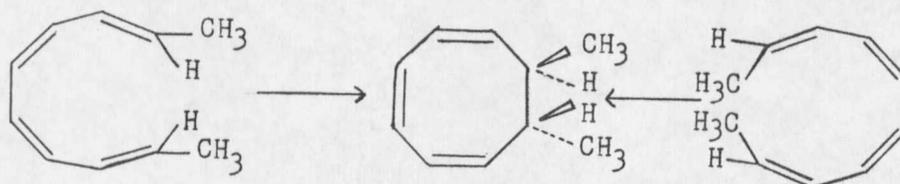
During the past ten to fifteen years norbornadiene (bicyclo-2,2,1-hepta-2,5-diene) has been shown to dimerize and trimerize when in the presence of various transition metals and excited thermally or photochemically. Some examples of the transition metal systems investigated with norbornadiene thermally are rhodium on carbon,<sup>1</sup> "bare" metals by reduction of nickel, cobalt, and iron acetylacetonates by triethyl aluminum,<sup>2</sup> nickel bisacrylonitrile,<sup>3</sup> zinc bistetracarbonylcobaltate,<sup>4</sup> dicobaltoctacarbonyl,<sup>5</sup> iron pentacarbonyl,<sup>6</sup> nickel tetracarbonyl,<sup>7</sup> cobalt tricarbonylnitrosyl,<sup>8</sup> and phosphine-substituted derivatives of the metal carbonyls. Fewer investigations have been pursued using photochemically excited metal systems in norbornadiene. Examples of these are chromium hexacarbonyl,<sup>9</sup> iron pentacarbonyl (or di-iron nonacarbonyl),<sup>10</sup> and substituted and unsubstituted-butadiene iron tricarbonyls.<sup>11</sup> The norbornadiene products obtained vary in type and amount depending on the transition metal used to catalyze the reaction.

Various intermediates have been postulated to explain the stereochemistry of the organic products. These intermediates have been based in part on isolated complexes of norbornadiene and in part on the stereochemistry necessary to coincide with that of the products. However, few attempts have been made to work out the details involved in determining what parameters are important to reach these postulated intermediates and from them to reach the products.

The isolation and characterization of intermediates is extremely helpful in determining reaction pathways of certain known reactants to form certain known products. Unfortunately, as in many reactions involving one or more fast steps the intermediates may be extremely unstable and cannot be isolated intact. Recently, some success has been obtained in isolating intermediates involved in hydrogenation of olefins. In one case, the complex  $\text{Ir}(\text{CO})\text{Cl}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ <sup>12</sup> was known to be square planar with the  $\text{P}(\text{C}_6\text{H}_5)_3$  group trans.<sup>13</sup> When hydrogen was added to a benzene solution of this complex a different complex was formed which when isolated was found to be  $\text{Ir}(\text{CO})\text{Cl}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{H}_2$ .<sup>14</sup> Its structure was found to be octahedral.<sup>15</sup> The subsequent reaction of  $\text{Ir}(\text{CO})\text{Cl}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{H}_2$  with an olefin in solution resulted in the same hydrogenated hydrocarbon as obtained in the original experiment.<sup>16</sup> Thus, one step was verified in this reaction. Although this type of intermediate yields much information about homogeneous catalysis very little of it can be directly applied to the cycloaddition reactions encountered with norbornadiene.

However, two important orbital symmetry theories have been reported, one by Woodward-Hoffmann<sup>17</sup> and the other by Mango,<sup>18</sup> which relate to specificity in stereochemistry in concerted organic and organometallic reactions. These theories neither answer the question of how to obtain an intermediate nor contribute to the kinetics but they do produce a basis on which intermediates could be reasonably postulated based on the conservation of orbital symmetry.

The first ideas to be presented in the literature regarding orbital symmetry restrictions on a generalized level were those of Woodward and Hoffmann. These ideas were first introduced in relation to electrocyclic reactions.<sup>19</sup> Electrocyclic reactions are defined as those reactions (forward or reverse) in which two  $\pi$  systems on the ends of a linear molecule combine to form a single  $\sigma$  bond. Many times in these reactions there is also either a double bond formed or double bonds rearranged within the molecule. An example of this type of reaction is the ring closure of decatetraenes thermally by conrotatory motion but photochemically by a disrotatory motion. The stereochemistry of the thermal reaction products is shown below.<sup>20</sup>



Orbital symmetry relationships were then incorporated into concerted intermolecular cycloaddition reactions which rationalized the stereochemistry maintained in these reactions.<sup>21</sup> An example of this type of reaction is the thermally excited reaction of cyclopentadiene and tropone to produce the tricyclic system as shown.<sup>22</sup>























































































































































































































































































