The Metallacyclopentane—Olefin Interchange Reaction

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Summary Tris(triphenylphosphine)tetramethylenenickel(II) and biscyclopentadienyltetramethylenetitanium, prepared from the reaction of a 1,4-dilithiobutane and the transition metal dihalides, react with olefins to produce substituted metallacyclopentanes; the stereochemistry and substitution pattern of the metallocycles formed from propene, octa-1,7-diene, and norbornadiene has been determined.

Metallacyclopentanes have been suggested as intermediates in a number of transition metal—olefin reactions. This type of complex has been prepared from 1,4-lithium or Grignard reagents, by the reaction of low-valent metals with strained olefins and by the insertion of low-valent metals into strained cyclobutanes. Owing to their unique geometry, these complexes are more stable than acyclic dialkyl metal complexes.

In our studies of nickelacyclopentanes, we found that 5-co-ordinate phosphine complexes decomposed to produce ethylene as the major product. To determine if this was a general reaction, an early transition element analogue was reinvestigated. A highly purified sample of biscyclopentadienyltetramethylenetitanium(IV) also produced ethylene as the major product. This and other results suggested that the metallocycles were in equilibrium with the bis-olefin complexes.

Exchange of the olefins in the bis-olefin complex would result in the formation of a new metallocycle. As seen in the Table, metallocyclopentanes can be produced in good yields by this method. Most of the metallocycles were characterized by acidolysis of the metal complex to produce the reduced dimer of the added olefin. Protonolysis has been demonstrated to give good quantitative results from simple metallocycles. As a further characterization, some of the complexes were carbonylated to cyclopentanone derivatives. This reaction has been found to be characteristic of metallocyclopentanes.

Table

<table>
<thead>
<tr>
<th>Complex</th>
<th>Olefin</th>
<th>[Olefin]/[Complex] (temp./°C)</th>
<th>Protonolysis product</th>
<th>Yield % based on the complex</th>
</tr>
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<tbody>
<tr>
<td>(I)</td>
<td>Octa-1,7-diene</td>
<td>68 (-5)</td>
<td>1,2-Dimethylcyclohexane</td>
<td>trans 97%</td>
</tr>
<tr>
<td>(I)</td>
<td>Propene</td>
<td>86 (-10)</td>
<td></td>
<td>cis 0%</td>
</tr>
<tr>
<td>(I)</td>
<td>Norbornadiene (NBD)</td>
<td>58 (0)</td>
<td>Hexane</td>
<td>53</td>
</tr>
<tr>
<td>(II)</td>
<td>Octa-1,7-diene</td>
<td>10 (-25)</td>
<td>2-Methylpentane</td>
<td>3</td>
</tr>
<tr>
<td>(II)</td>
<td>Propene</td>
<td>63 (-20)</td>
<td>2,3-Dimethylbutane</td>
<td>6</td>
</tr>
<tr>
<td>(II)</td>
<td>Octa-1,7-diene</td>
<td>10 (-25)</td>
<td>(Thermal) (NBD)</td>
<td>57</td>
</tr>
<tr>
<td>(II)</td>
<td>Propene</td>
<td>63 (-20)</td>
<td>1,2-Dimethylcyclohexane</td>
<td>trans 71%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>cis 23%</td>
</tr>
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</tbody>
</table>
The metallocycle (III) from the reaction of biscyclo­
pentadienyltetramethylenetitanium (II) and octa-1,7-
diene has been isolated and analysed. The $^{13}$C n.m.r.
spectrum of (III) was consistent with it being a mixture of
cis- and trans-isomers. Addition of carbon monoxide
produced a mixture of cis- and trans-hydrindanone in good
yield (Scheme). Attempts to isolate the metallocycle
formed from (I) and octa-1,7-diene resulted in recovery of
octa-1,7-diene, and production of 2-methylmethylene-cyclo-
hexane and nickel(0)-phosphine complexes. Spectroscopic
studies ($^{13}$C and $^1$H n.m.r.) were hampered by low solubility
and stability, and large P couplings. Treatment of this
complex with carbon monoxide produced trans-hydrindan­
one (no cis) in 78% yield together with the above decom­
position products.

The two complexes (I) and (II) differed in the stereo­
chemistry of the products formed with octa-1,7-diene. The
reaction of the titanium complex (II) produced a ca. 3:1
ratio of trans- to cis-isomer, reflected both in the $^{13}$C n.m.r.
spectrum, and carbynylation and protonolysis studies,
whereas the nickel complex (I) produced only the trans-
isomer as shown by protonolysis and carbynylation studies.
Thermal decomposition of the metallocycle produced from
norbornadiene produced the exo-trans-endo norbornadiene
dimer. This is analogous to the results obtained from the
nickel dipyridyl-norbornadiene metallocycle produced from
Ni$^{0}$ complexes.  

Of particular interest was the production of n-hexane as
the major dimer from the reaction of propene with either
complex. This suggests that the more stable isomer of the
metallocycle contains the alkyl groups adjacent to the
metal. The nickel complex was only stable below $-20^\circ$C
or under propene atmosphere and the titanium analogue
decomposed above $-50^\circ$C.

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† $^{13}$C($^1$H) n.m.r. spectrum of (III) at $-30^\circ$C: $^1$H 114.3 (Cp), 56.7 (Cd),
34.1 (CC, trans), 32.5 (Cc, cis), and 30.4 and 30.1 (Cb)
p.p.m. The shift for Cd is similar to that in a tantalum metallocycle (ref. 9).

7 R. H. Grubbs and A. Miyashita, unpublished results.