Exploring the Reaction Mechanism and Origin of Regioselectivity in Di-Nickel Catalyzed Alkyne Cyclotrimerization

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Why do we study first-row transition metal catalysts?

How much Pt, Pd, or Ni can you get for $5000 today?
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5.03 oz Pt  
6.73 oz Pd  
17,056 oz Ni  
0.533 US tons Ni
Previous Methods of Synthesis

- Reactivity of mono-metallic complexes has been studied extensively

- Comparatively little regioselectivity due to the stereochemistry around metal center

DOI: 10.1039/C6DT03389J
Previous Methods of Synthesis

- We know relatively little about the reactivity of bi-metallic complexes in comparison to our knowledge of mono-metallic complexes.

- The M-M distance, which can be controlled with the choice of ligand, offers alternate reactivity and selectivity over mono-metallic catalysts.

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Previous Methods of Synthesis

- Cotton reported that the above bi-metallic Nb and Ta complexes yielded mixtures of the 1,3,5 and 1,2,4-substituted benzenes

- Nagasawa expanded the reaction scope, showing the bi-Nb complex regioselectively forms the 1,3,5-substituted products with terminal alkynes

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What sparked interest

- Uyeda reported the regioselective synthesis of 1,2,4-substituted benzenes with a novel naphthyridine diimine-bridged di-nickel complex

DOI: [10.1021/jacs.5b04990](http://10.1021/jacs.5b04990)
Uyeda’s findings

- Found that this reaction heavily favored 1,2,4-substituted product
- Asked the question: Why?

DOI: 10.1021/jacs.5b04990
Our system

- Major difference between our ligand and Uyeda’s is that the xanthene backbone has a higher degree of flexibility than the naphthyridine backbone.

DOI: 10.1039/C6DT04532D
Basis Set Effects

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Ni-N (1)</th>
<th>Ni-N (2)</th>
<th>C-C (alkyne)</th>
<th>Imine C-C</th>
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<tr>
<td>6-31G(d)</td>
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<td>6-311G(d)</td>
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Differences in Spin Surfaces for Various Intermediates Relative to Singlet Surface

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<th>Basis set</th>
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<th>ΔH</th>
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Reactivity Findings

- We found the reactivity of our complex to be different than Uyeda’s.
- We did not have the same level of regioselectivity as Uyeda did, thus forming much more of the 1,3,5 isomer.
- We also produced cyclooctatetraene products.

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Suggested Causes

- One possible explanation for this divergent reactivity would be the flexibility of our ligand. The rigidity of Uyeda’s system causes very little change in the Ni-Ni distance, whereas our system allows for more variation in the Ni-Ni distance.

Ni-Ni: 2.560 Å
Ni-Ni: 2.534 Å
Current / Future work

- Investigate both electronic and other possible causes for the regioselectivity, or lack thereof, of our reaction