Asymmetric Cyclization of Ene-Allenes by Nickel Catalysis

General reaction:

\[
\text{[Ni(cod)] (10 mol\%)} \quad \text{dpdf or Xantphos (10 mol\%)} \quad \text{PhMe, 100 °C, argon}
\]

ene-allenes added over 10 min

45–95% yield when \( R^2 = \text{H} \)

cis-selective

or

49% yield when \( R^2 = \text{Me}, R_3 = \text{H}, X = \text{C(CO}_2\text{Et)}_2 \)

Selected examples:

- 83% yield
- 79% yield
- 64% yield
- 49% yield
- Reaction at distal \( \pi \)-bond

Mechanism of the [2+2]-cyclization pathway:

Significance: The [2+2] cycloaddition of ene-allenes is a powerful methodology in the construction of fused cyclobutanes. However, one of the challenges of known protocols is the limited substrate scope, tolerating only styrene or diene \( \pi \)-components. Alexian and Noucti demonstrate the utility of nickel catalysis in a stereoselective [2+2]-cycloaddition to generate diverse carbocyclic frameworks A.

Comment: It is noteworthy to point out the effectiveness of this protocol to cyclize terminal allenes which are not tolerated in other known methods. Moreover, an interesting observation was discovered where methyl substitution at \( R^2 \) changes the [2+2] cycloaddition from the proximal to the distal \( \pi \)-bond of the allene, generating the bicyclo[4.2.2] scaffold B instead.