

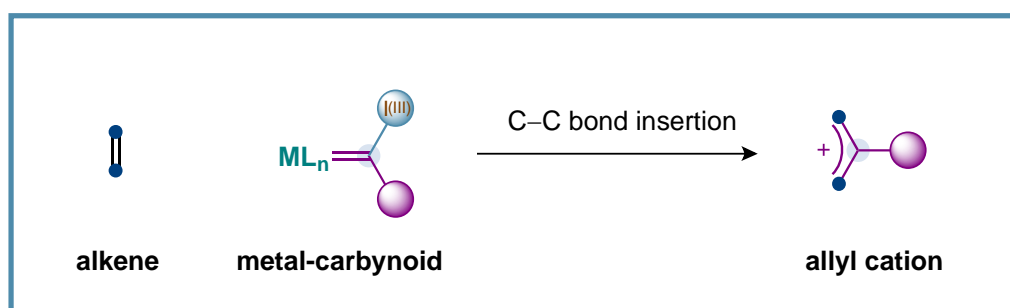
CATALYTIC CLEAVAGE OF C(sp²)-C(sp²) BONDS WITH METAL-CARBYNOIDS

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For more than half a century, the discovery of new metal-carbon bond-forming strategies has been cornerstone in the development of transition-metal catalysis. The catalytic generation of organometallic species with metal-carbon single/double bonds, such as metal-L (L = alkyl, alkenyl, alkynyl, aryl) or metal-carbene (metal=L) is widely used in reaction discovery and development. However, while metal-carbynes² – the organometallic species with a metal-carbon triple bond (metal≡L) –, have been key catalysts in alkyne metathesis³, their catalytic generation and general application in catalytic carbyne transfer processes has been largely unexplored, mainly due to the lack of suitable monovalent carbon sources. Surprisingly, methodologies circumventing this problem by generating metal-carbynoids have not been reported.

Herein, we report a catalytic strategy that generates metal-carbynoids by selective diazo activation of designed carbyne sources². We found that the metal-carbynoid species provoke C(sp²)-C(sp²) bond scission in alkenes by inserting a monovalent carbon unit between both sp²-hybridized carbons. The process access synthetically useful allyl cation intermediates following the Woodward-Hoffmann-DePuy rules.



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