

# H• Transfer from Transition-Metal Hydrides. Applications to Radical Polymerizations and Cyclizations

## Frontiers in Catalysis Science and Engineering Seminar Series

Presented by...

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#### Abstract

Steric as well as electronic factors affect the rate at which H• is transferred between a transition metal and the carbon of a double bond. However, the weak M–H bonds of the first-row metals, particularly vanadium, make them uniquely effective in this regard.

Such reactions can be used in the catalysis of *chain transfer* during radical polymerizations. In this process a metalloradical abstracts H• from a chain-carrying radical, transfers it to the double bond of a monomer, and starts a new chain. The resting state of traditional cobalt chain-transfer catalysts is the Co(II) metalloradical, but both the metalloradical and the hydride are present during the operation of newer (Cr) catalysts. Success at catalyzing chain transfer requires (1) that the M–H bond not be too much stronger than the 50 kcal/mol C–H bond in chain-carrying radicals, and (2) that M• be stable enough to discourage the formation of bonds other than that to hydrogen.

CpCr(CO)<sub>3</sub>H and HV(CO)<sub>4</sub>(P–P) can be used to initiate radical *cyclizations* by transferring H• to activated terminal olefins. However, the resulting radicals must cyclize quickly; competing reactions include transfer of a second H• (resulting in hydrogenation) and removal of an H• (resulting in isomerization). Cp(CO)<sub>3</sub>CrH is relatively slow at H• transfer, but can be regenerated with H<sub>2</sub> gas, enabling it to carry out reductive cyclizations catalytically; vanadium hydrides HV(CO)<sub>4</sub>(P–P) are faster but operate stoichiometrically.

#### More info?

<http://www.columbia.edu/cu/chemistry/fac-bios/norton/group/mpages/jnorton.html>

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