Studies on Heterobimetallic Complexes Containing Phosphinoethyl-, Aminoethyl-, and Diphenylphosphino-Functionalized Cyclopentadienyl Group VI Metal Carbonyl Fragments

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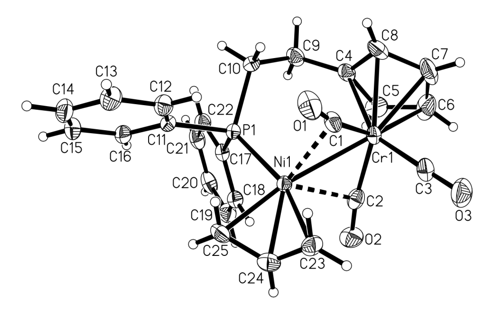
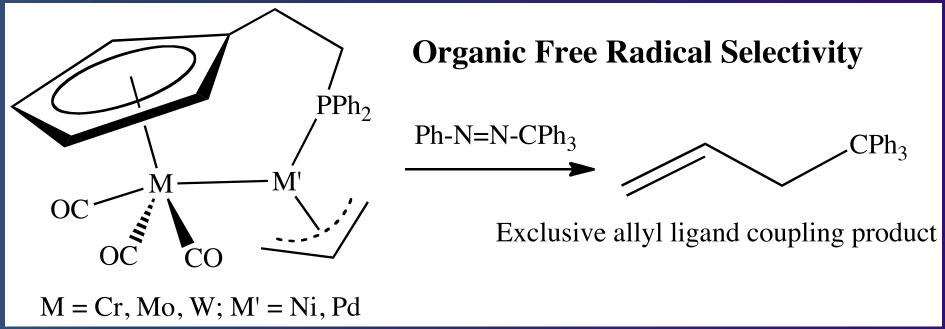
The (2-(diphenylphosphino)ethyl)cyclopentadienyl (Cp^{PPh}) ligand stabilizes $M\{M'(\eta^3\text{-allyl})\}(CO)_3(\mu\text{-}\eta^5\text{:}\eta^1\text{-}Cp^{PPh})$ ($M = Cr, Mo, W$; $M' = Ni, Pd$) for free radical reactivity studies.



Cr-Ni Complex

A modest heterobimetallic effect may render the chromium allyl complexes more reactive than the tungsten allyl complexes on the basis of ^{31}P NMR kinetic experiments.



Organic Free Radical Selectivity

Exclusive allyl ligand coupling product

M = Cr, Mo, W; M' = Ni, Pd

Heterobimetallic Allyl Ligand Conversion to 4,4,4-Triphenyl-1-butene on the basis of GC/MS (PAT = $PhNNCPh_3$, TD = trityl dimer)

¤	Cr¤		Mo¤		W¤	
¤	PAT¤	TD¤	PAT¤	TD¤	PAT¤	TD¤
Ni¤	71(1)¤	100¤	37.2(5)¤	72(2)¤	54.8(3)¤	87(3)¤
Pd¤	65.2(4)¤	100¤	42.0(1)¤	73(1)¤	50.6(9)¤	89(1)¤

While phenyl radical attack at Pd(II) is believed the first step in the trityl radical-allyl ligand coupling reaction of PAT and $Pd(\eta^3\text{-allyl})Cl(PPh_3)$, direct trityl radical attack at η^3-allyl is strongly suggested in these M-M' complexes.