ORGANOMETALLIC CHEMISTRY OF BIMETALLIC COMPOUNDS

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DISCLAIMER

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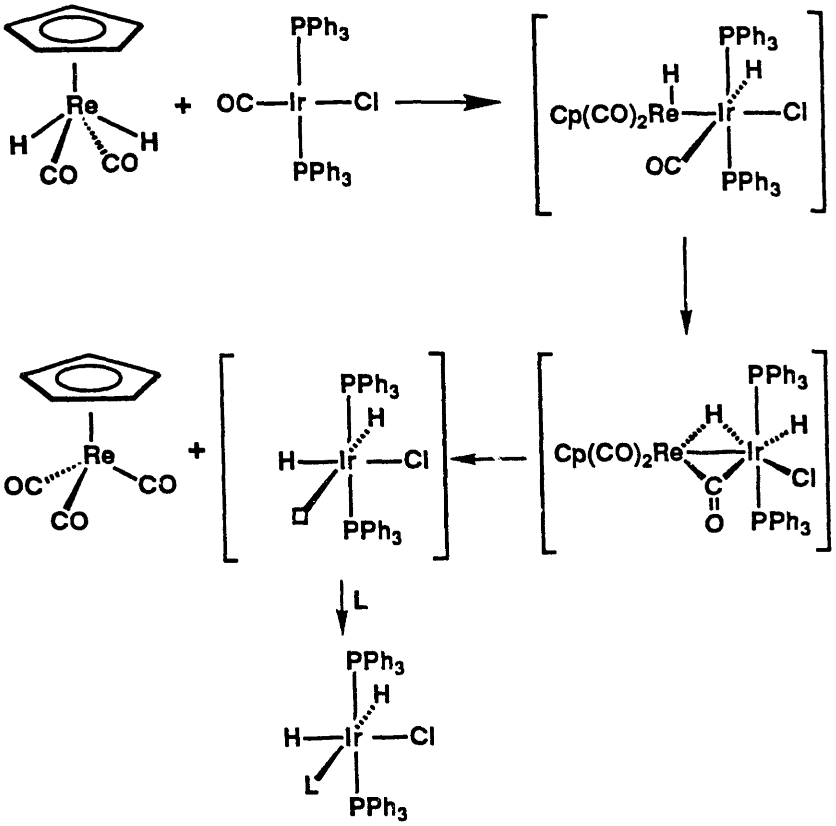
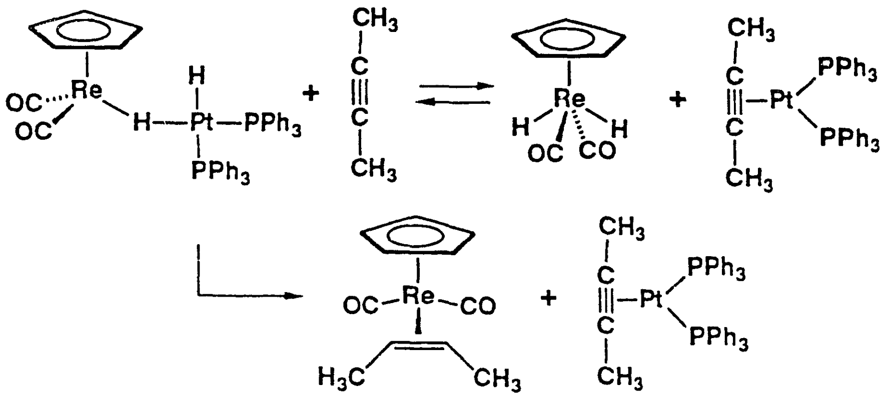
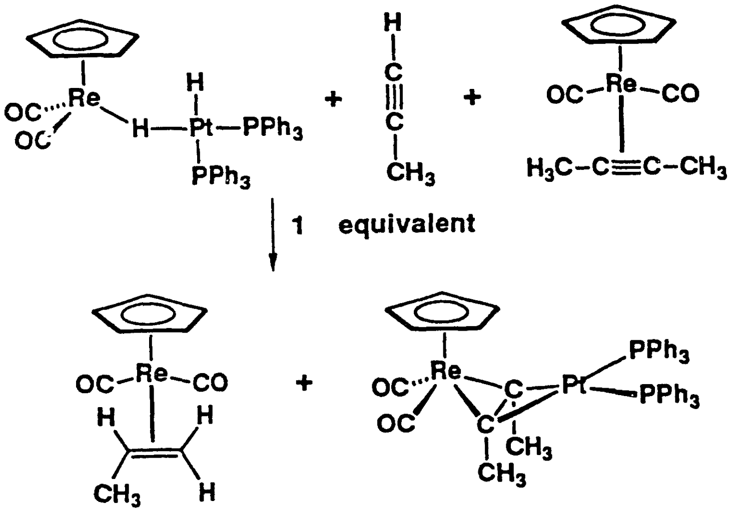
A. Heterobimetallic Dihydrides. A full paper describing hydrogen transfer form $Cp(CO)_2ReH_2$ to *trans*-$Ir(CO)(Cl)(PPh_3)_2$ via a heterobimetallic Re-Ir intermediate was published.[1]



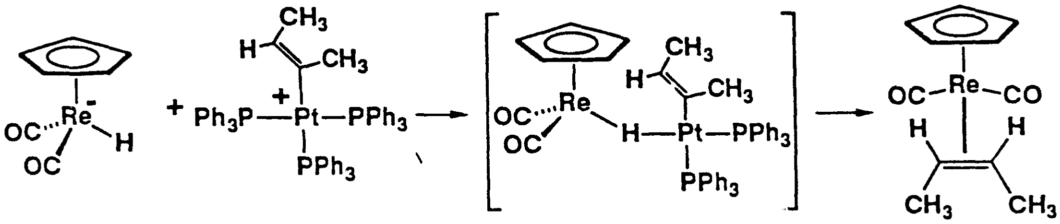
A communication describing the reaction of the rhenium-platinum dihydride complex $Cp(CO)_2Re(\mu\text{-}H)PtH(PPh_3)_2$ with alkynes was published.[2] The mechanism of this rare example of heterobimetallic catalysis is under active investigation.



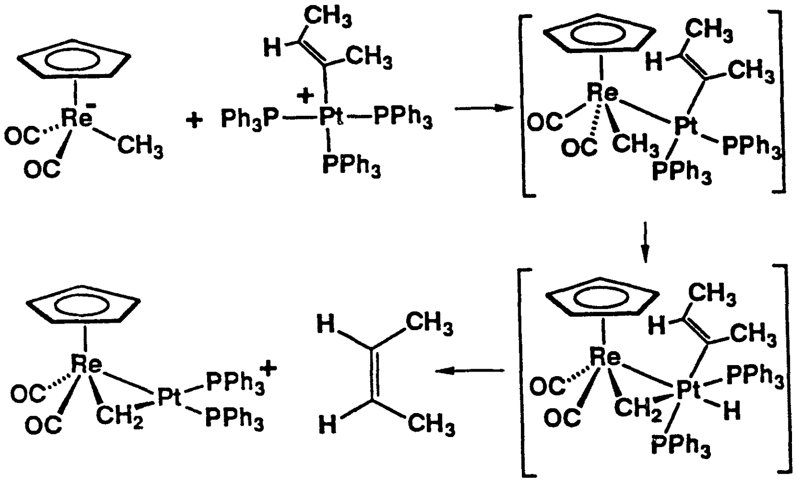
In the course of probing whether rhenium-alkyne complexes are intermediates in this reaction, we discovered the interesting RePt alkyne complex shown below.[3]



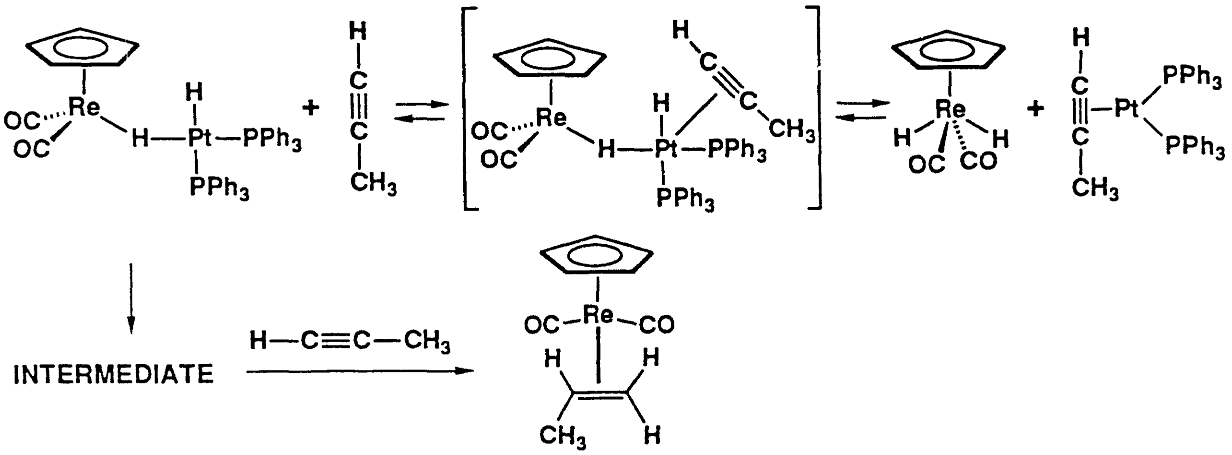
The reaction of Cp(CO)$_2$ReH$^-$ with cationic vinylplatinum(II) complexes was investigated as a possible route to a proposed RePt vinyl intermediate in the alkyne hydrogenation reaction. In agreement with the proposed mechanism, this reaction produced rhenium alkene complexes.[3]



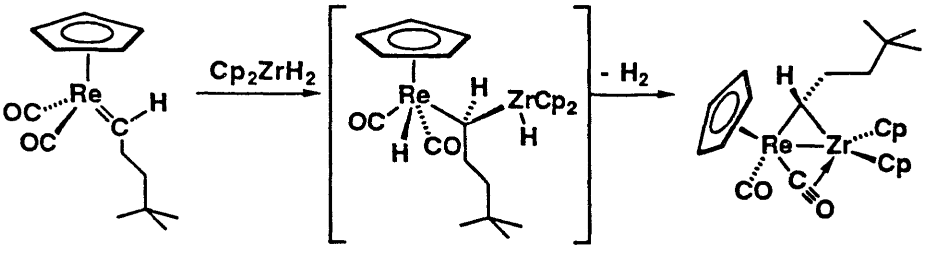
In an attempt to isolate a compound with a Re-Pt bond, the reaction of $Cp(CO)_2ReCH_3^-$ with vinylplatinum(II) compounds was studied. An interesting μ-CH_2 RePt compound was produced; the reaction is proposed to proceed as shown below with key steps involving Re-Pt bond formation and insertion of Pt into a C-H bond of the $ReCH_3$ group.[3]



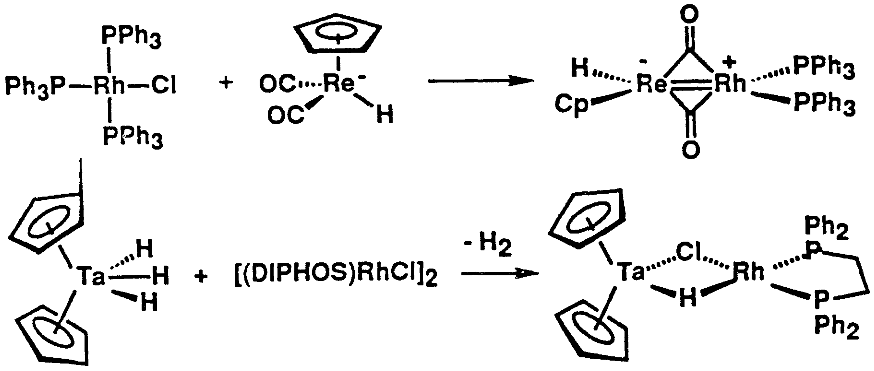
Kinetic investigations of the reaction of $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ with propyne have been initiated. We have found that increasing alkyne concentrations results in <u>slower</u> rates of reaction. To explain this, we propose that an equilibrium between $RePtH_2$ and $Cp(CO)_2ReH_2$ and $Pt(PPh_3)_2$(alkyne) is set up and that the slow step in the reaction is a unimolecular rearrangement of $RePtH_2$ to a reactive intermediate of unknown structure.[3]



B. **Early-Late Transition Metal Heterobimetallic Compounds.** We published a communication describing the syntheses of the Zr-Re μ-alkylidene complexes shown below by reaction of rhenium carbene complexes with Cp_2ZrH_2.[4]

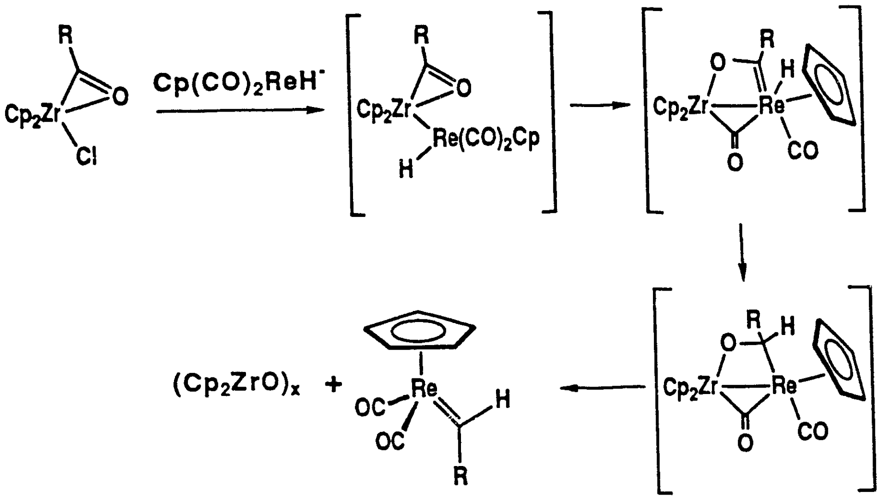


We also published the synthesis of TaRh and ReRh hydride complexes.[5]

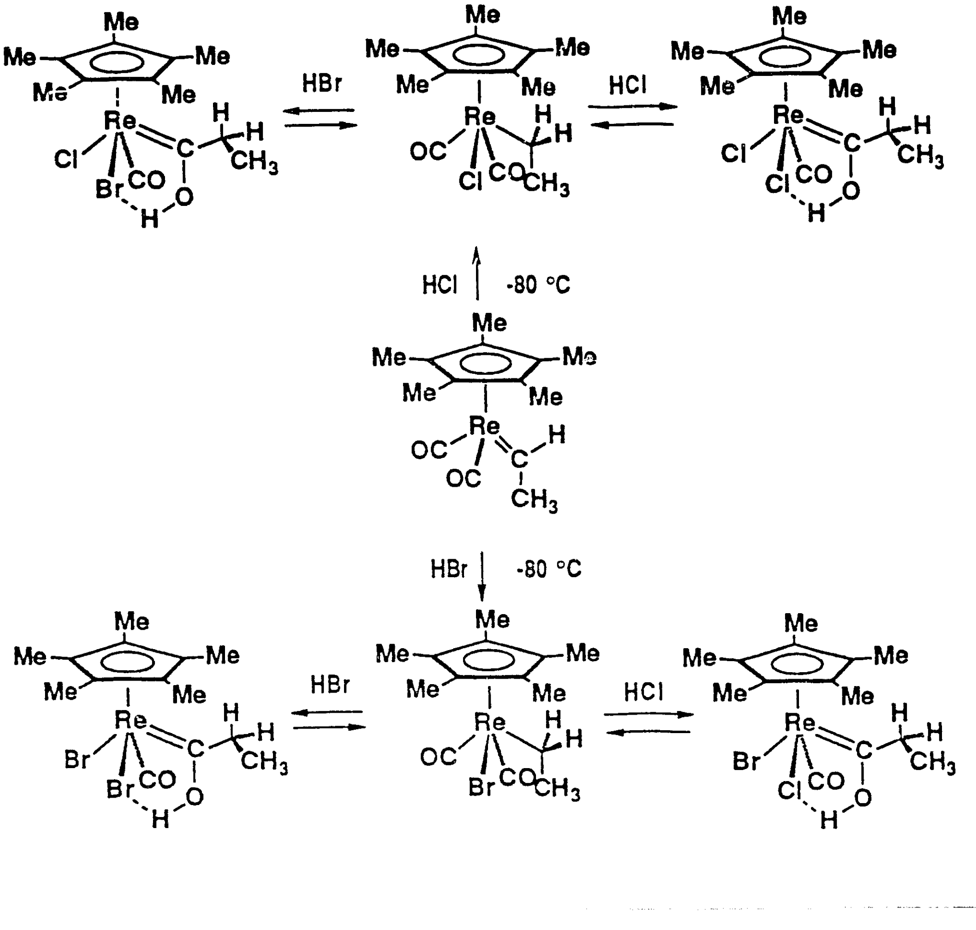


An article summarizing our work with ZrRu heterobimetallic compounds appeared in Volume 400 of the Journal of Organometallic Chemistry.[6]

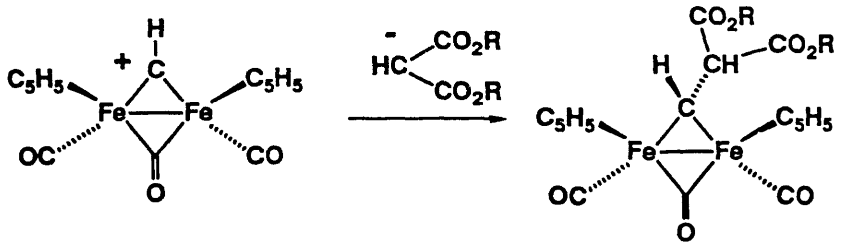
C. **Amphiphilic Carbene Complexes and Hydroxycarbene Complexes.** The reaction of $Cp(CO)_2ReH^-$ with $Cp_2Zr(\eta^2\text{-}COR)Cl$ produced the new rhenium carbene complex $Cp(CO)_2Re{=}CHR$.[7]



The amphiphilic carbene complex $Cp^*(CO)_2Re{=}CHCH_3$ reacts with excess HCl to reduce and chain extend the carbene ligand.[8] The reaction is stereospecific: the reaction of HCl followed by HBr produces a different isomer than HBr followed by HCl.

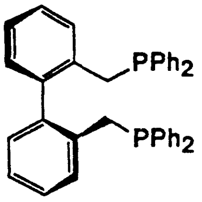


D. **Diiron compounds with Bridging Hydrocarbon Ligands.** A study of the reactions of the bridging methylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+$ with carbon and heteroatom nucleophiles has been published.[9]

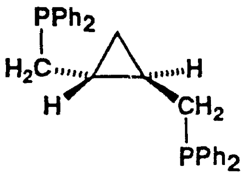


E. **Diphosphine Chelates with Natural Bite Angles near 120°.** We have defined the "natural bite angle" of a chelating diphosphine as the preferred chelation angle determined only by ligand backbone constraints and not by metal valence angles. We have used molecular mechanics to calculate the natural bite angle of chelates and to estimate their flexibility.[10] We are particularly interested in ligands with wide natural bite angles near 120°. Such ligands should preferentially occupy equatorial sites in trigonal bipyramids.

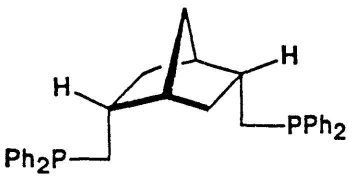
Three of the ligands we have studied in detail are BISBI, T-BDCP, and the norbornyl diphosphine shown below which we recently designed and synthesized.[11]



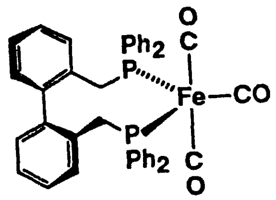
BISBI

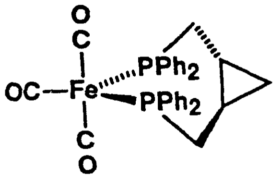


T-BDCP

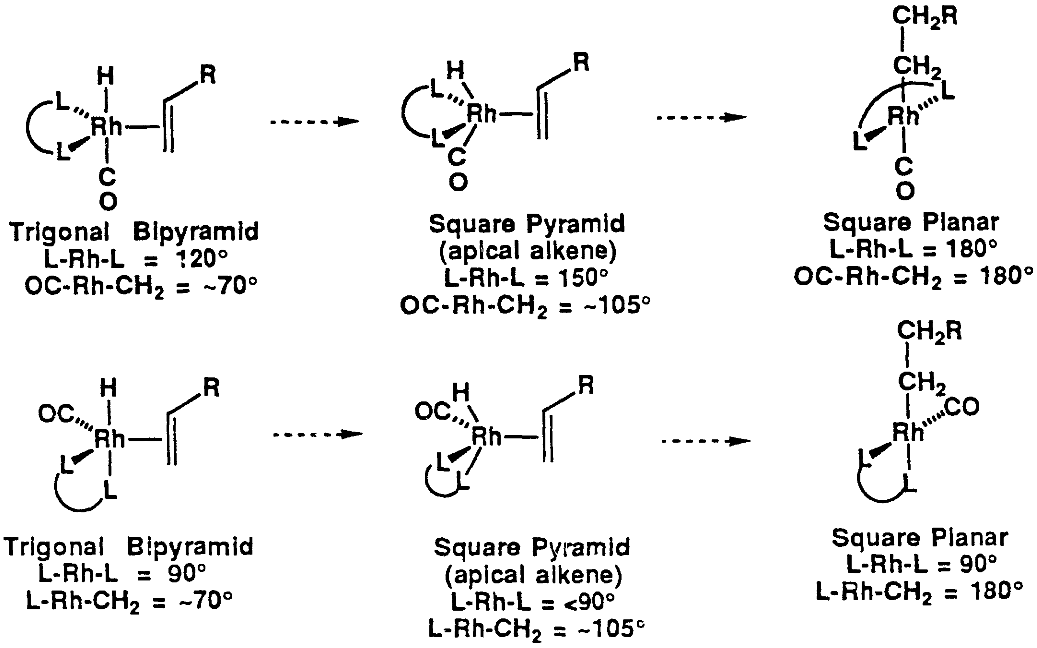


We have compared our calculated natural bite angles with observed bite angles for $(CO)_3Fe$(diphosphine) complexes.[12] The observed bite angles are systematically larger than the calculated natural bite angles but the calculations indicate that the ligands are relatively flexible.





We have employed a series of chelating diphosphines with wide bite angles as ligands in rhodium catalyzed hydroformylation.[13] A rough correlation between the regioselectivity of linear aldehyde formation and the size of the natural bite angle of chelating diphosphines was found.



Trigonal Bipyramid
L-Rh-L = 120°
OC-Rh-CH_2 = ~70°

Square Pyramid
(apical alkene)
L-Rh-L = 150°
OC-Rh-CH_2 = ~105°

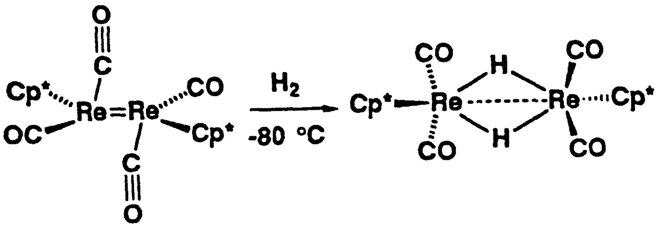
Square Planar
L-Rh-L = 180°
OC-Rh-CH_2 = 180°

Trigonal Bipyramid
L-Rh-L = 90°
L-Rh-CH_2 = ~70°

Square Pyramid
(apical alkene)
L-Rh-L = <90°
L-Rh-CH_2 = ~105°

Square Planar
L-Rh-L = 90°
L-Rh-CH_2 = 180°

F. **Synthesis and Reactions of M=M Compounds.** We recently discovered that Cp*(CO)$_2$Re(THF) can be isolated as a solid and that the solid is converted quantitatively to the M=M dimer Cp*(CO)$_2$Re=Re(CO)$_2$Cp*.[14] This unusual dimer of two 16e-d^6 fragments is stable at room temperature but reacts with H$_2$ at -80 °C to produce Cp*(CO)$_2$Re(μ-H)$_2$Re(CO)$_2$Cp*.



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