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ORGANOMETALLIC CHEMISTRY OF BIMETALLIC COMPOUNDS

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Overview. Four main projects at the interface between organometallic chemistry and homogeneous catalysis were pursued. All were designed to give increased understanding of the mechanisms of organometallic reactions related to homogeneous and heterogeneous catalysis. In addition, a minor study involving η^5- to η^1-cyclopentadienyl ring slippage in catalysis was completed.

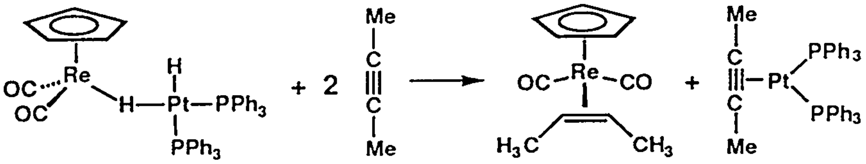
I. Heterobimetallic Dihydrides. Bimetallic catalysis has almost unlimited potential but very few systems are known in which there is direct evidence for involvement of a bimetallic compound. Our discovery that $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ hydrogenates alkynes to give rhenium-alkene complexes provided a rare example of bimetallic catalysis amenable to detailed kinetic and mechanistic studies. Progress in gaining a relatively full understanding of this reaction is detailed below.

II. Chelating Diphosphines with Wide Natural Bite Angles Near 120° were used to make catalysts in which phosphine ligands are constrained to diequatorial positions in trigonal bipyramids. The effect of chelate bite angle on the regioselectivity of Rh catalyzed hydroformylation was explored in detail. Wide bite angle chelates give very high n : i regioselectivity of aldehyde formation. This selectivity has been shown by deuterioformylation studies to be determined in the largely irreversible addition of a Rh-H to a complexed alkene.

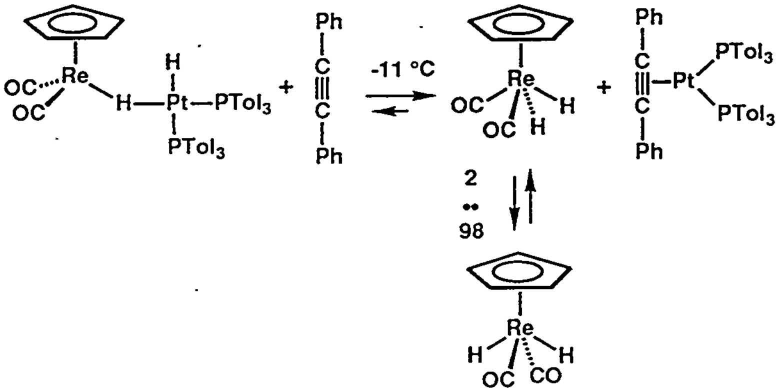
III. Synthesis and Reactions of M=M Compounds. Our recent discovery of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$, the second example of a dimer of d^6-16e fragments and of its reversible reaction with H_2 to produce $Cp^*(CO)_2Re(\mu\text{-}H)_2Re(CO)_2Cp^*$ have opened a new area of research. The basic reactions of Re=Re are being studied. The wide range of different reactions with alkynes will be detailed below.

IV. Reactions of the Unsaturated 46e Cluster $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$. In the course of reinvestigating Schneider's claimed synthesis of $C_5Me_5Co{=}CoC_5Me_5$, we discovered that the majority of his material was actually $(C_5Me_5)_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$. We have investigated the rich chemistry of this reactive 46e cluster and will concentrate here on the reaction with acetylene that produces the bis-alykylidyne complex $(C_5Me_5)_3Co_3(\mu_3\text{-}CCH_3)_2$.

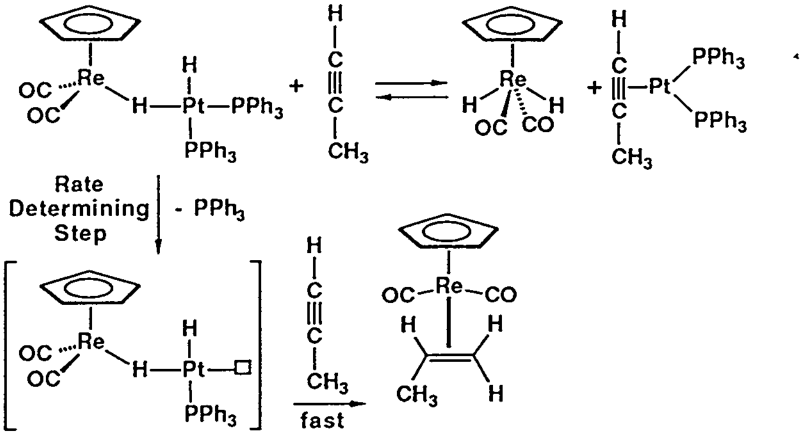
I. Heterobimetallic Dihydrides. Our detailed investigations of the mechanism of the hydrogenation of alkynes by the heterobimetallic compound $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ which produces rhenium alkene complexes, have led to several interesting discoveries. A summary of our progress in these investigations has been published.[193]



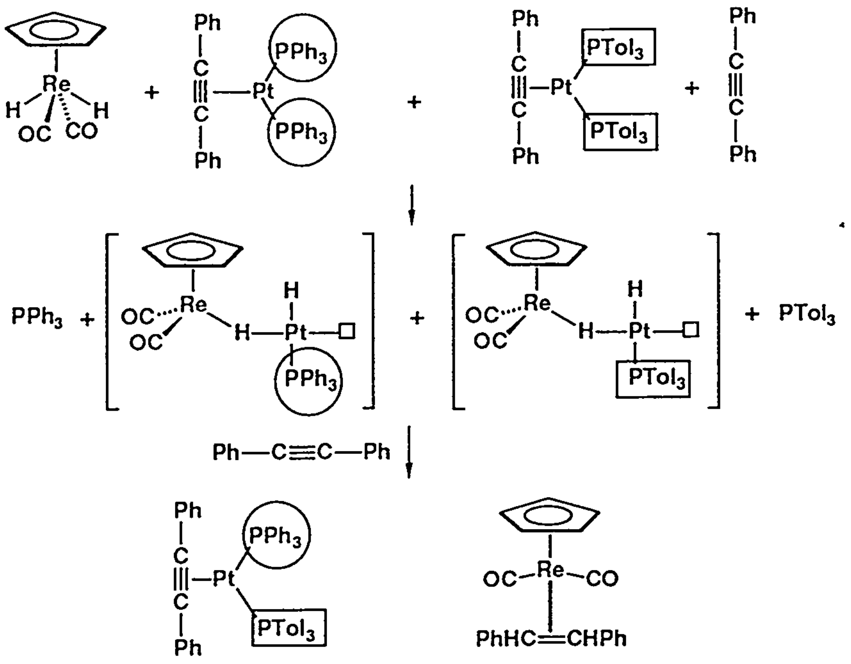
The initial reaction of $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ with alkynes produced *trans*-$C_5H_5(CO)_2ReH_2$ and (alkyne)$Pt(PPh_3)_2$. A least motion pathway should have produced *cis*-$C_5H_5(CO)_2ReH_2$ initially. We have now found that *cis*-$C_5H_5(CO)_2ReH_2$ can be produced by protonation of $C_5H_5Re(CO)_2H^-$ at low temperature and that *cis*-$C_5H_5(CO)_2ReH_2$ rapidly rearranges to *trans*-$C_5H_5(CO)_2ReH_2$ at room temperature. *cis*-$C_5H_5(CO)_2ReH_2$ was also observed as the initial product in the low temperature reaction of $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ with alkynes.[189]



Kinetic investigations of the reaction of $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ with propyne have shown that increasing alkyne concentrations results in slower rates of reaction. A good fit of the kinetic data was obtained with a kinetic model involving somewhat faster equilibration of $Cp(CO)_2ReH_2$ and $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$, and rate determining unimolecular conversion of $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ to a reactive intermediate committed to alkene complex formation. Higher concentrations of alkyne deplete the concentration of $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ by shifting the equilibrium towards $Cp(CO)_2ReH_2$ and $(CH_3C{\equiv}CH)Pt(PPh_3)_2$; this lowers the concentration of $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ and results in slower rates. The leading candidate for the reactive intermediate formed in the rate determining step is $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)$, formed by unimolecular dissociation of PPh_3 from $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$.[193]

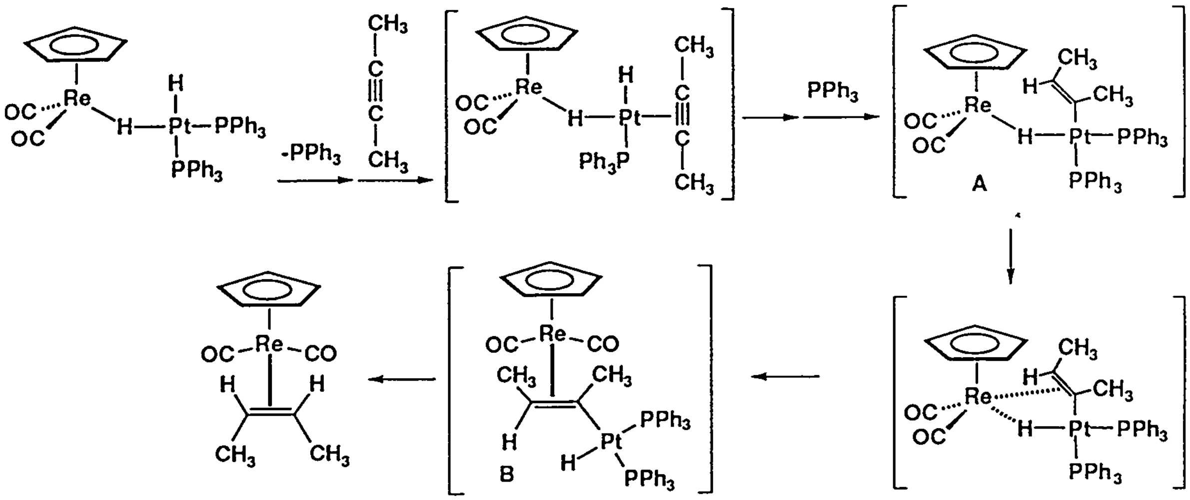


Rate determining formation of the reactive intermediate $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)$ by PPh_3 dissociation makes the risky prediction that the rates of alkyne reduction and phosphine exchange will be closely correlated. Every time $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)$ is generated, alkyne reduction occurs and an opportunity for phosphine exchange at platinum is created. The system we chose to test this mechanistic hypothesis was the reaction of *trans*-$Cp(CO)_2ReH_2$ with PhC≡CPh catalyzed by a mixture of the two symmetrically labeled alkyne platinum complexes, $(PhC{\equiv}CPh)Pt(PPh_3)_2$ and $(PhC{\equiv}CPh)Pt(PTol_3)_2$. In order for the exchange experiment to be meaningful, the two different phosphine labeled unsaturated intermediates must be generated at comparable rates. We found that the $PTol_3$ complex catalyzed the hydrogenation of PhC≡CPh 4.3 times faster than the PPh_3 complex.[193]

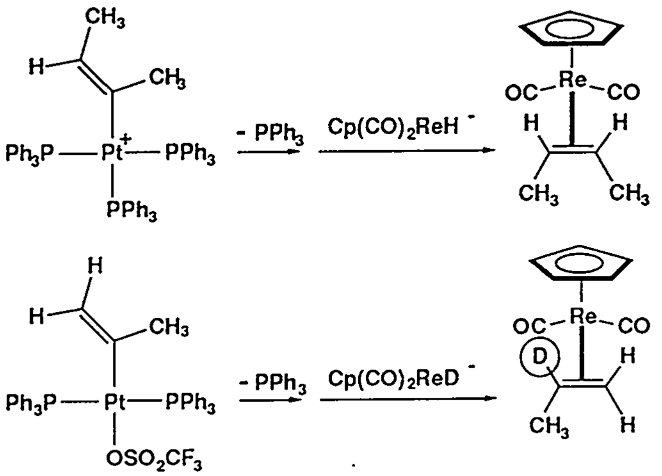


During the first 20 % conversion of PhC≡CPh (0.13 M) and $Cp(CO)_2ReH_2$ (0.13 M) to $Cp(CO)_2Re(PhHC{=}CHPh)$ catalyzed by a mixture of $(PhC{\equiv}CPh)Pt(PPh_3)_2$ (0.031 M) and $(PhC{\equiv}CPh)Pt(PTol_3)_2$ (0.023 M), the relative rate of hydrogenation to give $Cp(CO)_2Re(PhHC{=}CHPh)$ and of formation of mixed phosphine complex $(PhC{\equiv}CPh)Pt(PPh_3)(PTol_3)$ was 1 : 0.53. The ratio predicted by our mechanistic model was calculated to be 1 : 0.37 taking into account the relative amounts of the starting platinum complexes, the relative rates of hydrogenation catalyzed by the two platinum complexes, and the relative amounts of free phosphine cogenerated with the coordinatively unsaturated reactive intermediates. Our calculated ratio of 1 : 0.37 is in good agreement with the observed ratio of 1: 0.53. This experiment supports our mechanistic hypothesis that the rate determining step in alkyne hydrogenation is PPh_3 dissociation from $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$.[193]

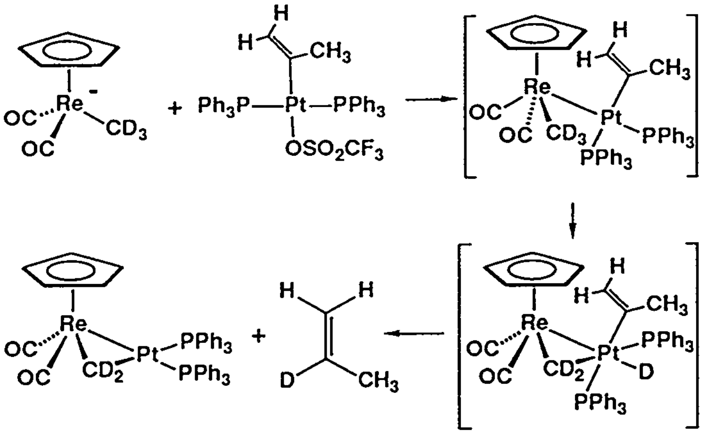
A modification of our initial mechanistic hypothesis for alkyne reduction by $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ takes into account kinetic evidence that the rate determining step probably involves PPh_3 dissociation. Cis addition of Pt-H across a complexed alkyne ligand is suggested to produce a vinyl platinum intermediate **A**. Next, simultaneous transfer of the vinyl ligand to rhenium and hydride to platinum would produce intermediate **B**. Finally, reductive elimination from the platinum center of **B** would produce a rhenium alkene complex with overall cis addition of H_2.



In an attempt to generate the proposed rhenium platinum vinyl intermediate **A**, the reaction of $K^+Cp(CO)_2ReH^-$ with $(PPh_3)_3Pt[(E)\text{-}C(CH_3){=}CHCH_3]^+CF_3SO_3^-$ in CD_3CN at 17 °C was studied. Although **A** was not directly observed, the expected product of its further reaction, the rhenium alkene complex $Cp(CO)_2Re(cis\text{-}CH_3CH{=}CHCH_3)$ was formed quantitatively.[182] Thus, the risky prediction of Re-alkene complex formation with retention of vinyl stereochemistry was borne out, consistent with our hypothesis that **A** is a precursor of rhenium alkene complexes.



We thought that by replacing the reactive hydride of intermediate **A** with a methyl group we might be able to observe the related methyl intermediate $Cp(CO)_2(CH_3)RePt[C(CH_3){=}CH_2](PPh_3)_2$ and establish the possibility of Re-Pt bond formation. Reaction of $Cp(CO)_2ReCH_3^-Li^+\cdot THF$ with *trans*-$(PPh_3)_2Pt[C(CH_3){=}CH_2](O_3SCF_3)$ in THF led to the isolation of the heterobimetallic μ-methylene complex $Cp(CO)_2Re(\mu\text{-}CH_2)Pt(PPh_3)_2$ as an air stable yellow solid in 54% yield.[184] To account for the formation of $Cp(CO)_2Re(\mu\text{-}CH_2)Pt(PPh_3)_2$, we proposed that initial formation of intermediate $Cp(CO)_2(CH_3)RePt[C(CH_3)=CH_2](PPh_3)_2$ is followed by insertion of platinum into a CH bond of the rhenium methyl group to give a rhenium hydride intermediate. Reductive elimination of the vinyl group and hydride from platinum then produces the observed μ-methylene complex.

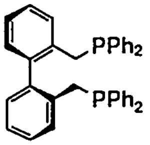
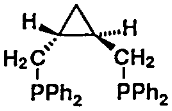
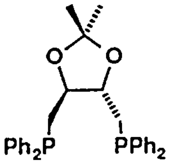
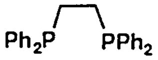


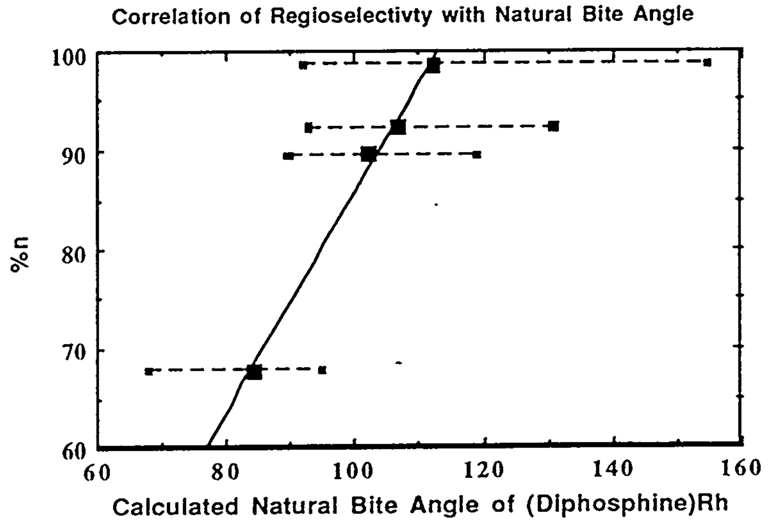
Overall, our kinetic studies have given a good description of mechanistic steps prior to rate determining loss of PPh_3 from $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ and our model compound studies have given insight into steps following the rate determining step. In the renewal proposal, we will outline approaches to designing catalytic alkyne reductions using the insight gained from the study of this stoichiometric bimetallic reduction of alkynes to rhenium-alkene complexes. The major obstacle is finding a system that will allow release of the product alkene while still accomplishing the requisite reduction.

II. Hydroformylation with Chelating Diphosphines with Wide Natural Bite Angles Near 120°. Chelating diphosphines with large P-M-P bite angles near 120° are interesting in the development of catalysts with controlled local geometry. The ability to systematically change the bite angle of a diphosphine chelate allows variation and possibly control of the selectivity of catalytic systems. Diphosphines with bite angles near 90° are very common and have been useful in studying metal complexes with phosphines locked into cis positions in octahedral and square-planar complexes or spanning an equatorial and apical site in a trigonal bipyramid. However, few chelating diphosphines with a preferred bite angle near 120° designed to selectively occupy diequatorial sites in trigonal bipyramids have been available for studying metal complexes.

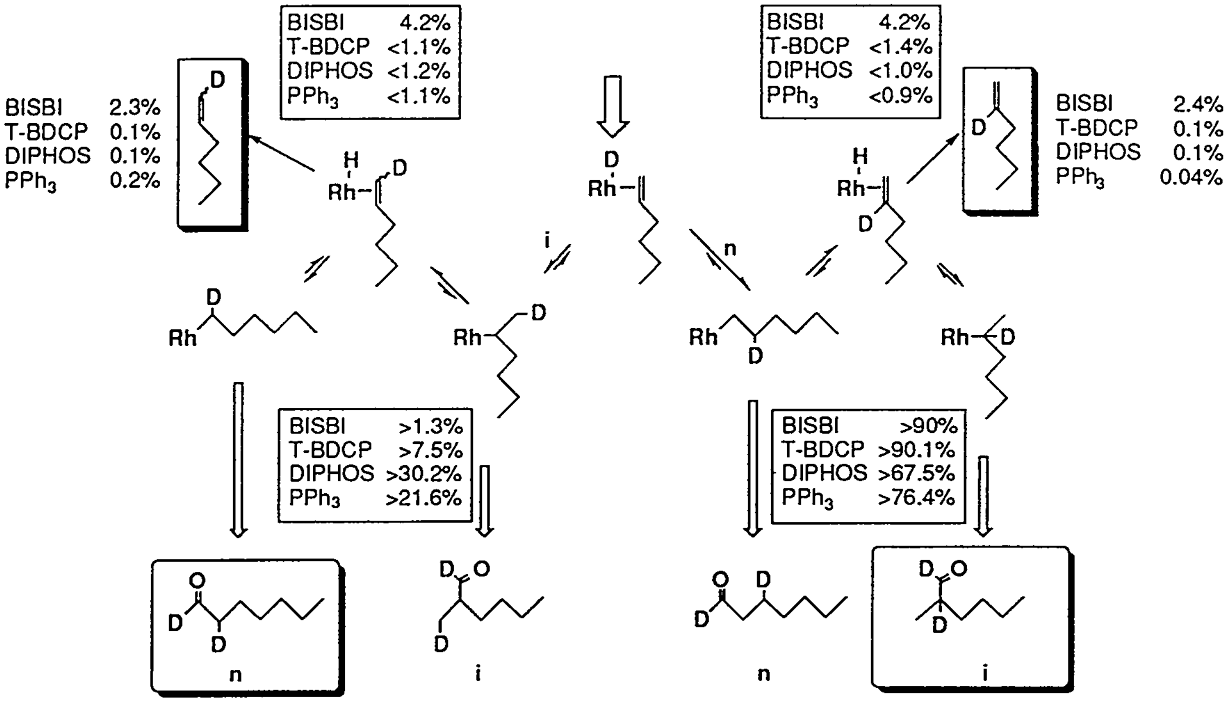
In rhodium catalyzed hydroformylation, the key $HRh(CO)_2L_2$ catalysts are known to be mixtures of diequatorial diphosphine and equatorial-apical diphosphine complexes. We thought that very different regioselectivity might be obtained for diphosphine catalysts in which the phosphines were constrained to diequatorial or to equatorial-apical coordination geometries. Therefore we carried out a study of the hydroformylation of 1-hexene using a series of chelating diphosphines having variable natural bite angles. In a full paper, we reported a strong correlation between high n : i regioselectivity in hydroformylation and wide natural bite angles of chelating ligands.[177]

Hydroformylation of 1-Hexene with Rh Diphosphine Catalysts

		Turnover Rate $[RCHO]\ [Rh]^{-1}\ h^{-1}$	n : i	β_n Bite angle	Ligand Flexibility
	BISBI	29.4	66.5	112.6	92°- 155°
	T-BDCP	3.7	12.1	106.6	93° - 131°
	DIOP	6.4	8.5	102.2	90° - 119°
	DIPHOS	1.1	2.1	84.5	68° - 95°



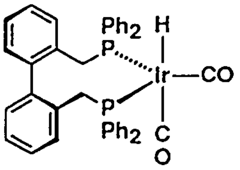
To test the hypothesis that regiochemistry is determined in the conversion of a rhodium(hydride)(alkene) complex to a rhodium alkyl complex, we studied the deuterioformylation of 1-hexene. We have found that the observed high selectivity for straight chain aldehydes is due to kinetic formation of a primary alkyl rather than equilibration of rhenium primary and secondary alkyls prior to hydroformylation. [C. P. Casey and L. M. Petrovich, unpublished results.]



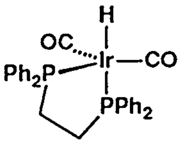
	n	i	n	i
BISBI	1.9%	1.4%	91.9%	0.03%
T-BDCP	<0.9%	7.6%	91.3%	<0.1%
DIPHOS	<0.7%	30.6%	68.2%	<0.3%
PPh_3	<0.8%	21.7%	77.1%	<0.2%

Test for Reversibility of Alkyl Rhodium Formation in the Presence of Phosphine Ligands. Percentages in Boxes are estimated amount of reaction that must pass thorough a particular intermediate.

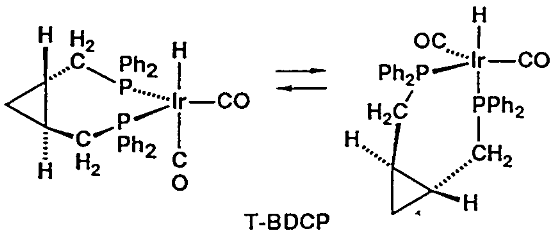
We have also prepared and determined the solid state and solution structures of (chelate)Ir$(CO)_2$H complexes as models for the key intermediate, (chelate)Rh(CO)(alkene)H, in rhodium catalyzed hydroformylation. Interestingly, the BISBI complex is locked into a diequatorial chelate, the DIPHOS complex is locked into a equatorial-apical chelate, and the T-BDCP ligand is an equilibrating mixture of both geometric isomers. [C. P. Casey and L. M. Petrovich, unpublished results.]



BISBI



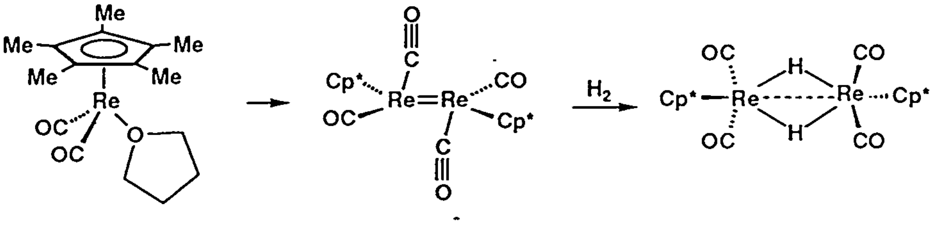
DIPHOS



T-BDCP

Since the regiochemistry of hydroformylation is determined in the conversion of a trigonal bipyramidal rhodium(hydride)(alkene) complex to a square planar rhodium alkyl complex and this requires a change in chelate geometry, chelate flexibility may be an important parameter in this regiochemical determining step. In the renewal proposal, we will outline our unsuccessful attempts to use molecular mechanics to develop a steric effects explanation for the high n : i regioselectivity seen for diequatorial chelates. We will also propose experiments to probe whether diequatorial and apical-equatorial chelates exert their control over regioselectivity via differing electronic properties.

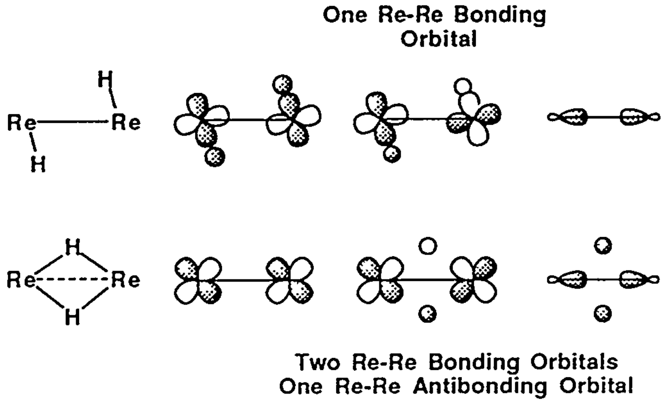
III. Synthesis and Reactions of M=M Compounds. In 1991, we reported the serendipitous synthesis of $Cp^*(CO)_2Re=Re(CO)_2Cp^*$ from decomposition of solid $Cp^*(CO)_2Re(THF)$ at room temperature.[180] The X-ray crystal structure of $Cp^*(CO)_2Re=Re(CO)_2Cp^*$ shows a 2.72 Å Re=Re double bond supported only by semibridging carbonyl ligands. $Cp^*(CO)_2Re=Re(CO)_2Cp^*$ is only the second example of a M=M bond between two d^6-16e fragments. Ordinarily, a dimer of two symmetric d^6-16e fragments would be expected to have a triplet electronic state with degenerate π^* orbitals, but the C_5Me_5 group and the semibridging carbonyl groups serve to break the degeneracy of the π^* orbitals. Fenske-Hall molecular orbital calculations carried out in collaboration with Bruce Bursten at Ohio State indicate that the Re=Re double bond can be described in terms of $\sigma^2,\pi^4,\delta^2,\delta^{*2},\pi^{*2}$ metal-metal bonding.[197]



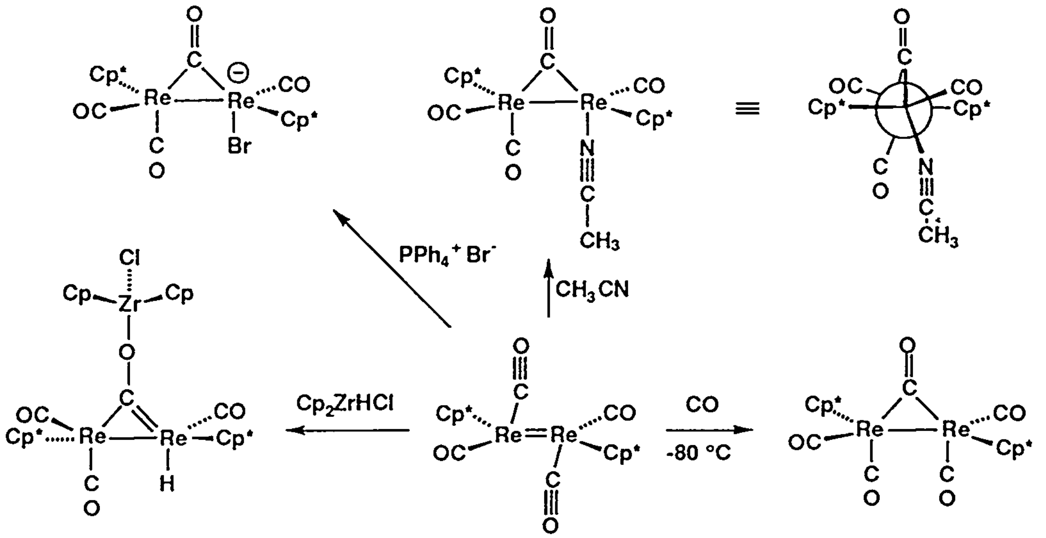
$Cp^*(CO)_2Re=Re(CO)_2Cp^*$ is thermally stable to over 100 °C but is kinetically extremely reactive. Addition of H_2 occurs within seconds at -80 °C to produce $C_5Me_5(CO)_2Re(\mu\text{-}H)_2Re(CO)_2C_5Me_5$.[180] Upon heating at 100 °C,

$C_5Me_5(CO)_2Re(\mu\text{-}H)_2Re(CO)_2C_5Me_5$ releases H_2 and reforms $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$.[191] Green reported the only previous example of the reversible thermal addition of H_2 to a metal-metal multiple bond in his studies of $[W(C_5H_4R)Cl_2(\mu\text{-}H)]_2$ [M. L. H. Green and P. Mountford, *J. Chem. Soc., Chem. Commun.* 732 (1989)].

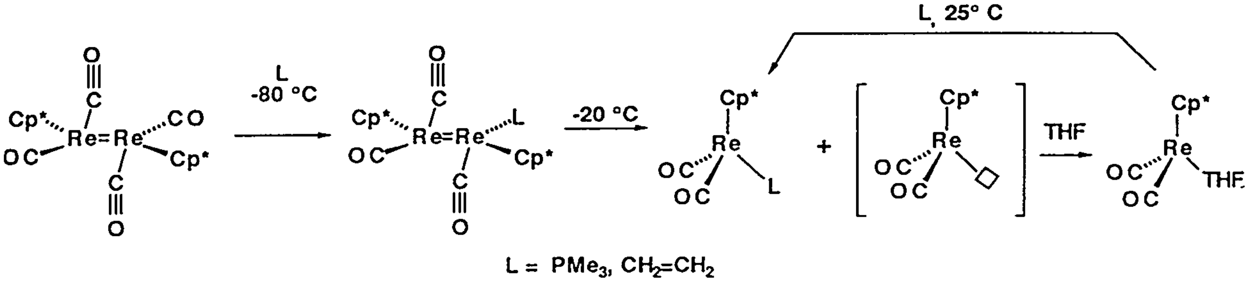
The X-ray crystal structure of $C_5Me_5(CO)_2Re(\mu\text{-}H)_2Re(CO)_2C_5Me_5$ shows a Re-Re distance of 3.143 Å indicative of a single bond.[180] We were surprised to find bridging hydrides since a structure with terminal hydrides would have an 18 electron count at each metal center, but the presence of two bridging hydrides normally implies the existence of two three center two electron M-H-M bonds and thus a greater than 18 electron count at each metal center. Our Fenske-Hall molecular orbital calculations have resolved the nature of the unusual metal-metal bonding in this case. our calculations indicate the presence of two 3 center-2e M-H-M bonds and a weak M-M antibond which gives a net M-M bond order of one. [C. P. Casey and G. P. Niccolai, unpublished results.]



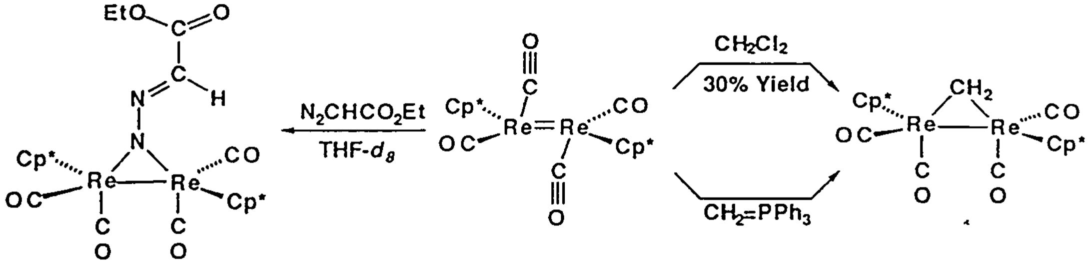
$C_5Me_5(CO)_2Re{=}Re(CO)_2C_5Me_5$ is extremely reactive toward most ligands. Reaction with CO occurs within seconds at -80 °C to produce the stable pentacarbonyl complex $C_5Me_5(CO)_2Re(\mu\text{-}CO)Re(CO)_2C_5Me_5$.[180] Stable 1 : 1 adducts are also obtained from reaction with Br^-, $NCCH_3$, and Cp_2ZrHCl. [C. P. Casey, H. Sakaba, R. S. Carino, and P. Kiprof, unpublished results.]



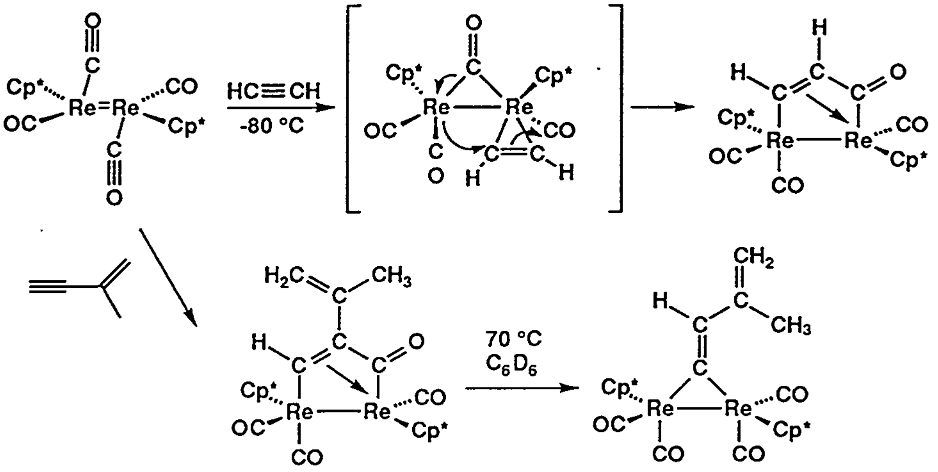
The reactions of $C_5Me_5(CO)_2Re{=}Re(CO)_2C_5Me_5$ with either PMe_3 or ethylene in THF produce a 1 : 1 adducts at low temperature, but at room temperature the adducts fragment to $Cp^*Re(CO)_2L$ and $Cp^*Re(CO)_2(THF)$. Our working hypothesis for these reactions involves initial coordination of an incoming ligand to one metal center along with bridging of a CO ligand. We are still exploring the factors that determine the stability and the mode of fragmentation of these adducts. [C. P. Casey, H. Sakaba, and R. S. Carino, unpublished results.]



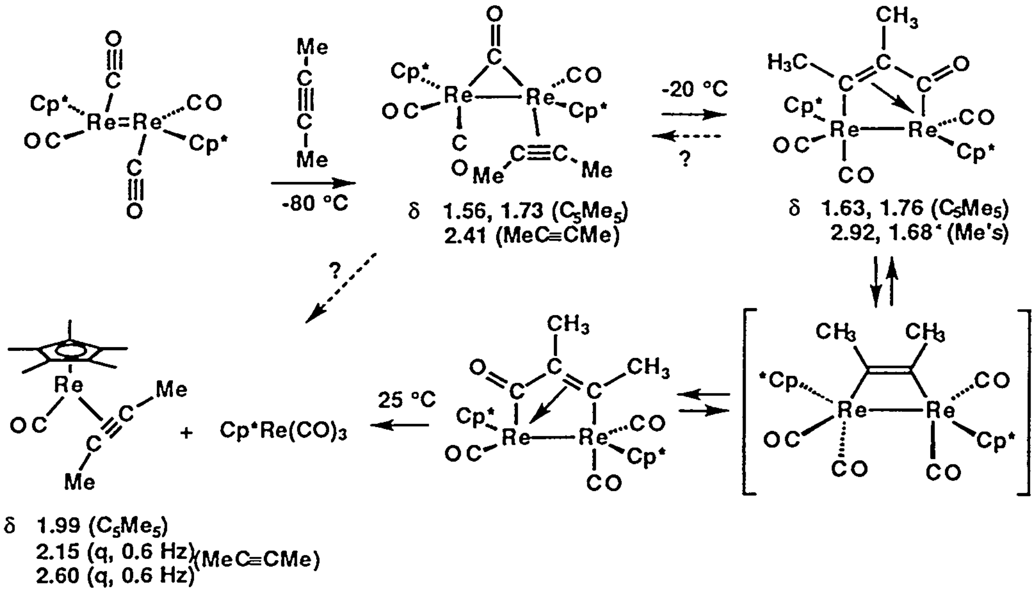
Other interesting reactions of $C_5Me_5(CO)_2Re{=}Re(CO)_2C_5Me_5$ have been observed with either CH_2Cl_2 or with $CH_2{=}PPh_3$ which both produce the bridging methylene complex $C_5Me_5(CO)_2Re(\mu\text{-}CH_2)Re(CO)_2C_5Me_5$. Reaction with ethyl diazoacetate produced the intriguing nitrogen bridged compound shown below. [C. P. Casey, H. Sakaba, and P. Kiprof, unpublished results.]



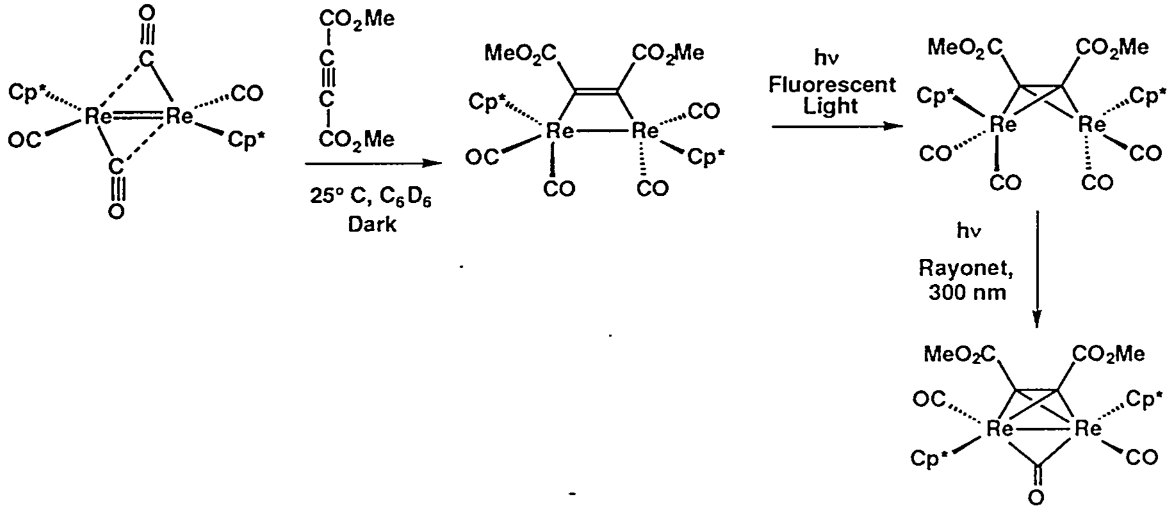
Reactions of alkynes with $C_5Me_5(CO)_2Re{=}Re(CO)_2C_5Me_5$ have proven to be particularly fascinating and diverse. HC≡CH reacts with $C_5Me_5(CO)_2Re{=}Re(CO)_2C_5Me_5$ rapidly at -80 °C to produce a dimetallacyclopentenone complex in which acetylene has been inserted between Re and a carbonyl ligand. Reaction of the enyne $HC{\equiv}C{-}CMe{=}CH_2$ produces a similar adduct which was characterized by X-ray crystallography;^{199} upon heating to 80 °C this dimetallacyclopentenone rearranges to the μ-vinylidene complex $C_5Me_5(CO)_2Re(\mu\text{-}C{=}CHCMe{=}CH_2)Re(CO)_2C_5Me_5$.



The reaction of $CH_3C{\equiv}CCH_3$ proceeds through a succession of intermediates. At -80 °C an unsymmetric 1 : 1 adduct is observed by NMR and is assigned a structure similar to that of 1 : 1 adducts with ligands such as CO or $NCCH_3$. This adduct rearranges to a dimetallacyclopentenone structure at -20 °C; coalescence of the Me and Cp* resonances of the dimetallacyclopentenone occurs at 10 °C probably via an unobserved dimetallacyclobutene intermediate similar to one isolated from DMAD. At room temperature the adduct fragments to the $C_5Me_5Re(CO)_3$ and the monocarbonyl 4-electron donor alkyne complex. [C. P. Casey, H. Sakaba, and R. S. Carino, unpublished results.]

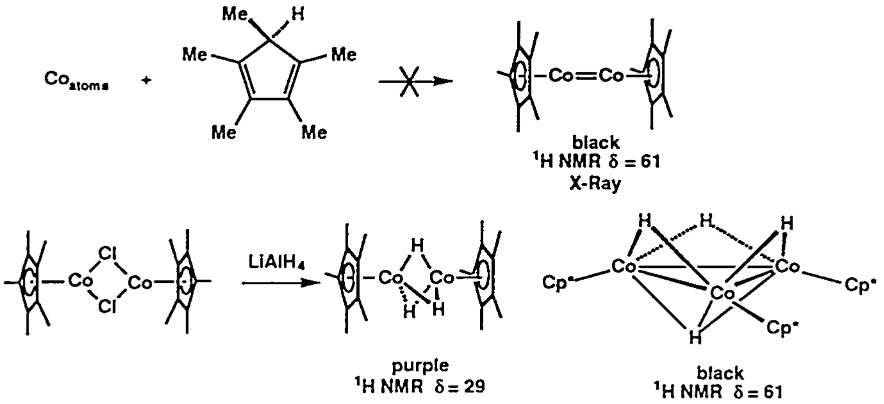


The reaction of $MeO_2CC{\equiv}CCO_2Me$ (DMAD) with $C_5Me_5(CO)_2Re{=}Re(CO)_2C_5Me_5$ also produces an exciting series of structures. The initial product is a dimetallacyclobutene that is converted under fluorescent room light to the butterfly structure in which each alkyne π-face is coordinated to a $C_5Me_5(CO)_2Re$ group. Ultraviolet photolysis brings about decarbonylation of the butterfly structure and formation of a bridging carbonyl adduct. All three of these compounds have been characterized by X-ray crystallography. The butterfly structure and the dimetallacyclobutene equilibrate at 80 °C. [C. P. Casey and R. S. Carino, unpublished results.]



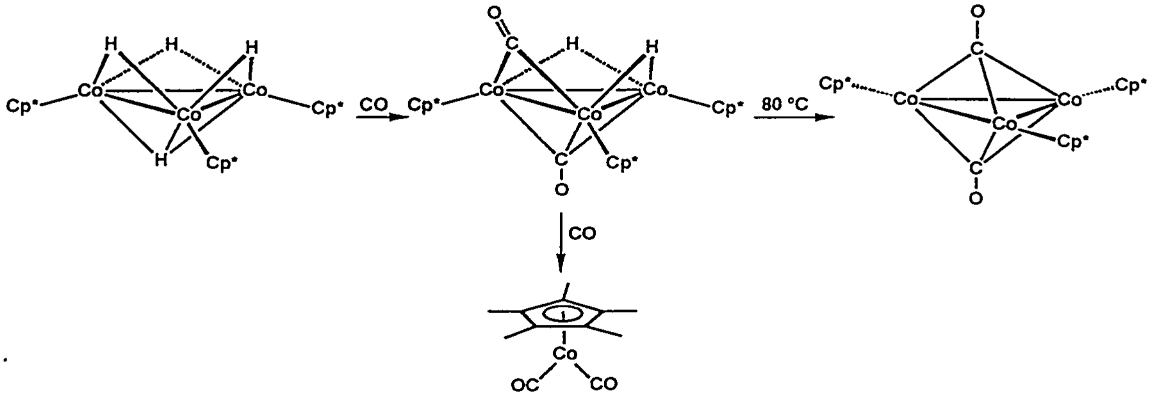
IV. Reactions of the Unsaturated 46e Cluster $Cp^*{}_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$. Because of our experience with the unusual and highly reactive Re=Re compound $C_5Me_5(CO)_2Re{=}Re(CO)_2C_5Me_5$, we were particularly struck by Schneider's report of $C_5Me_5Co{=}CoC_5Me_5$, a compound possessing a metal-metal double bond without any supporting ligands [J. J. Schneider, R. Goddard, S. Werner, C. Krüger, *Angew. Chem. Int. Ed. Engl.* **1991**,*30,* 1124]. This compound obtained from reaction of cobalt atoms with pentamethylcyclopentadiene in a metal atom reactor seemed so unusual that we reinvestigated its structure. In particular, its paramagnetism conflicted with simple electron counting and its failure to react with CO was totally unexpected. MO calculations on $C_5H_5Co(\mu\text{-}H)_{0\text{-}4}CoC_5H_5$ (collaboration with Bruce Bursten) indicated that $C_5H_5Co{=}CoC_5H_5$ should be diamagnetic but that $C_5H_5Co(\mu\text{-}H)_{3\text{ or }4}CoC_5H_5$ should be paramagnetic.^{183}

Synthetic and X-ray structural studies (collaboration with Klaus Theopold at University of Delaware) demonstrated that Schneider's structural assignment was incorrect. Our joint publication with Theopold pointed out that (1) the black compound reported by Schneider and having a paramagnetic ^1H NMR chemical shift of δ 61 is actually the tricobalt compound $(C_5Me_5)_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$; (2) the compound Schneider studied by X-ray crystallography is $(C_5Me_5)Co(\mu\text{-}H)_3Co(C_5Me_5)$ and has δ 29 and (3) both compounds react with CO to produce $C_5Me_5Co(CO)_2$ and H_2.^{187}

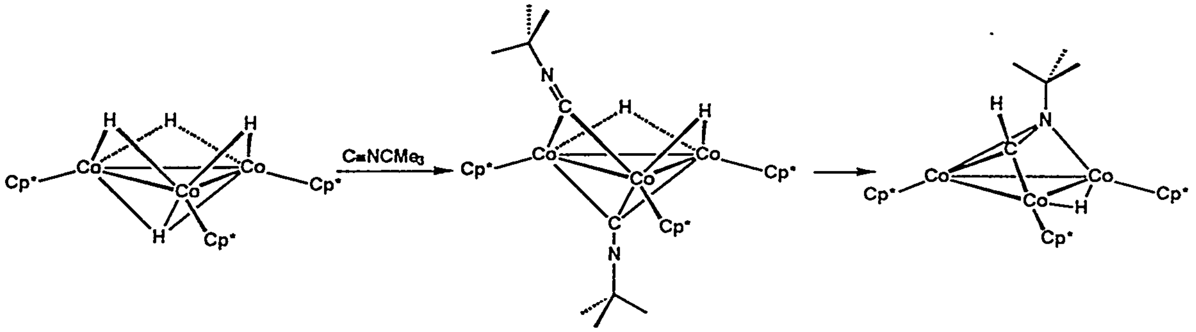


The synthetic studies carried out in conjunction with the structure reassignment of $C_5Me_5Co{=}CoC_5Me_5$ gave us ready access to $(C_5Me_5)_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$. This 46 electron paramagnetic tricobalt cluster is very reactive and has an interesting chemistry that we have begun to explore. In establishing the structure of $(C_5Me_5)_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$, we found that it reacted with excess CO to release H_2 and produce $Cp^*Co(CO)_2$. The reaction of $Cp^*{}_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$ with only two equivalents of CO forms the biscarbonyl dihydride cluster

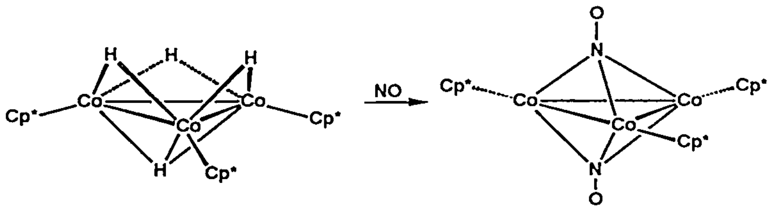
$Cp^*_3Co_3(\mu_3\text{-}CO)(\mu_2\text{-}CO)(\mu\text{-}H)_2$.[194] Reaction with additional CO produces $Cp^*Co(CO)_2$ quantitatively. Upon heating at 80 °C, $Cp^*_3Co_3(\mu_3\text{-}CO)(\mu_2\text{-}CO)(\mu\text{-}H)_2$ loses H_2 to form the paramagnetic compound $Cp^*_3Co_3(\mu_3\text{-}CO)_2$. The reaction of $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$ with $CNCMe_3$ leads to the reduction of the isonitrile and formation of $Cp^*_3Co_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}HC{=}NCMe_3)$.[202]



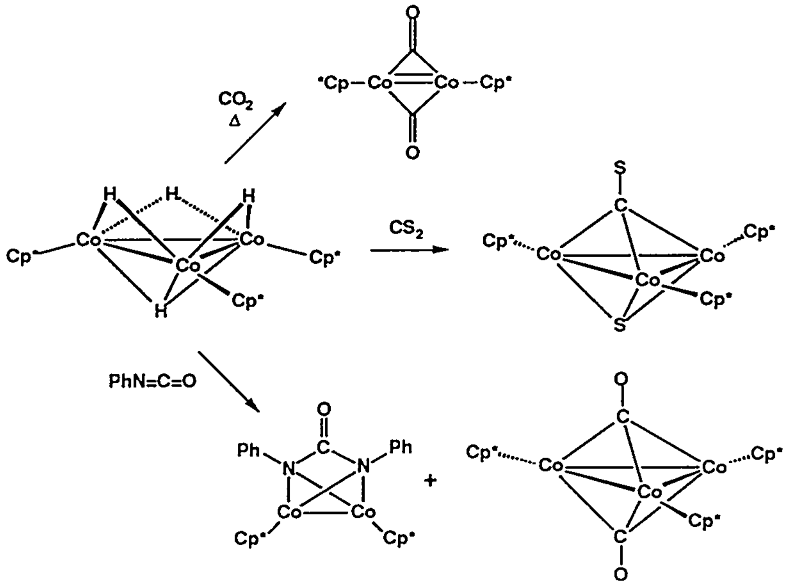
Because isocyanides are isoelectronic with CO, it was not unexpected that reaction of *tert*-butyl isocyanide with $(C_5Me_5)_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$ at -35 °C produced $Cp^*_3Co_3(\mu_3\text{-}CNCMe_3)(\mu_2\text{-}CNCMe_3)(\mu\text{-}H)_2$, an analog of the CO product. Surprisingly, this initial adduct undergoes a facile insertion of the isocyanide into a cobalt-hydrogen bond to produce the 48 electron formimidoyl cluster $Cp^*_3Co_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}HC{=}NCMe_3)$.[194]



In an effort to prepare a 48 electron analog of the 46 electron paramagnetic compound $Cp^*_3Co_3(\mu_3\text{-}CO)_2$, we studied the reaction of $Cp^*_3Co_3(\mu\text{-}H)_4$ with NO which produced the 48 electron diamagnetic complex $Cp^*_3Co_3(\mu_3\text{-}NO)_2$ which was characterized by X-ray crystallography.[192]

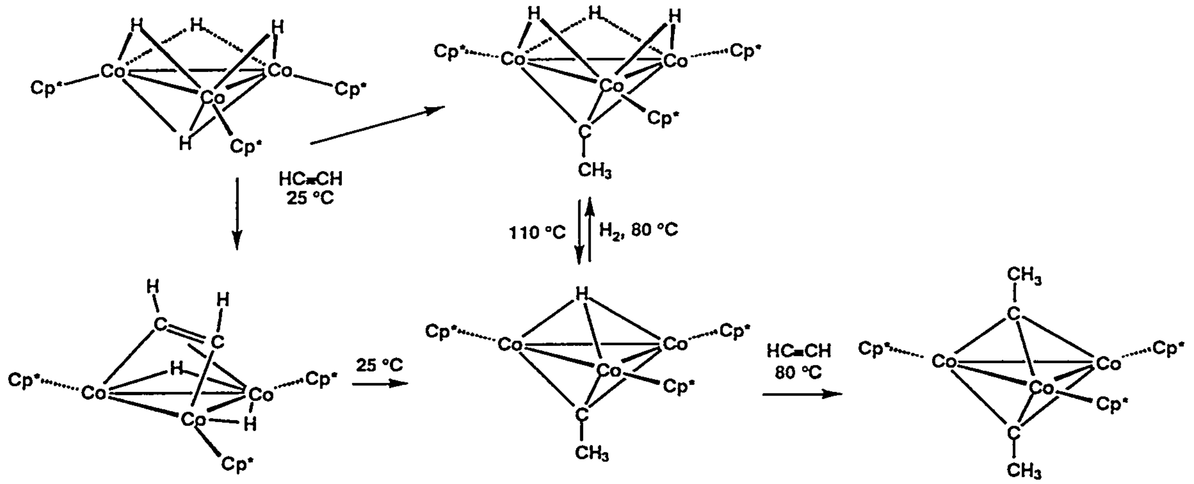


The reaction of the paramagnetic tetrahydride cluster $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$ with CO_2 and with the CO_2 analogs CS_2, and PhN=C=O gives products resulting from cleavage of a C=X bond. Reaction with CO_2 occurred only upon heating to 120 °C and produced $Cp^*Co(\mu\text{-}CO)_2CoCp^*$. Reaction with CS_2 occurred at room temperature to give a mixture of products including $Cp^*_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$. Reaction with PhN=C=O gave a 1 : 2 ratio of the paramagnetic dicarbonyl tricobalt cluster $Cp^*_3Co_3(\mu_3\text{-}CO)_2$ and a dicobalt bridging urea complex $Cp^*Co(\mu\text{-}PhNCONPh)CoCp^*$. [C. P. Casey and R. A. Widenhoefer, unpublished results.]

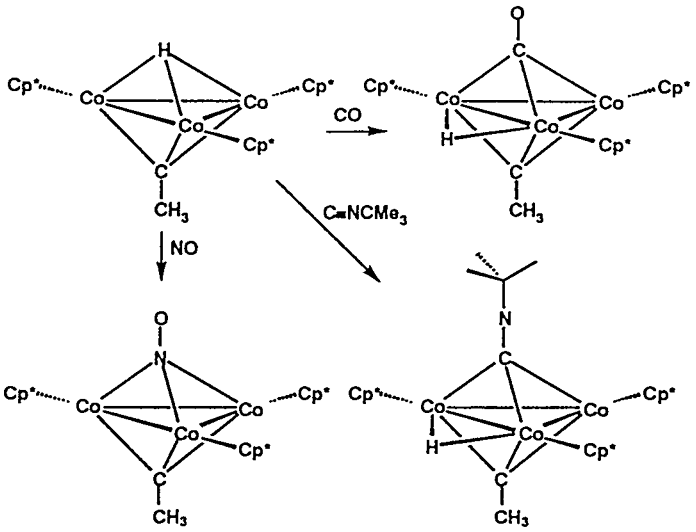


The most interesting and significant reaction of the paramagnetic tetrahydride cluster $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$ is with acetylene which led ultimately to the formation of a bis ethylidyne cluster $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$.[195] Since this transformation is related to the conversion of acetylene to μ-ethylidyne ligands on metal surfaces, we have begun detailed studies of its mechanism. Two intermediates were isolated during the course of the reaction: the diamagnetic monoethylidyne trihydride and $Cp^*_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}CCH_3)$ and the paramagnetic monoethylidyne monohydride $Cp^*_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCH_3)$. X-Ray crystal structures of these two ethylidyne clusters pointed out a misassignment of the cluster formed from thermolysis of

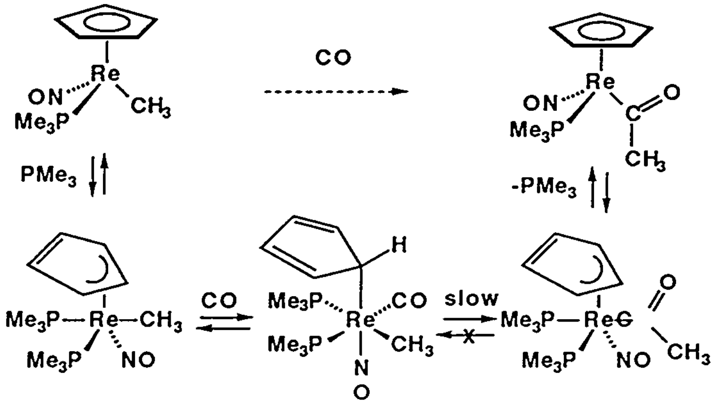
$Cp^*Co(H_2C{=}CH_2)_2$.[198] These two intermediates are kinetic products but can be interconverted at higher temperatures. At lower temperature, a third intermediate $Cp^*_3Co_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2,\eta^1,\eta^1\text{-}HC{=}CH)$ has been detected by ^1H NMR spectroscopy and its conversion to the paramagnetic monoethylidyne monohydride $Cp^*_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCH_3)$ has been monitored. [C. P. Casey, S. L. Hallenbeck, and R. A. Widenhoefer, unpublished results.] In the renewal proposal, detailed deuterium labeling studies to determine the types of intermediates involved in this important transformation will be outlined.



The paramagnetic monoethylidyne monohydride $Cp^*_3Co_3(\mu_3\text{-}H)(\mu_3\text{-}CCH_3)$ is very reactive towards a wide range of ligands. It reacted with CO to form the 1 : 1 carbonyl ethylidyne adduct $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}CO)(\mu_2\text{-}H)$, with *tert*-butyl isocyanide reacted to form the 1 : 1 isocyanide ethylidyne adduct $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}CNCMe_3)(\mu_2\text{-}H)$, and with NO to formed the nitrosyl ethylidyne cluster $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}NO)$.[200]



V. η^5- to η^1-Cyclopentadienyl Ring Slippage in Catalysis. We have found that PMe$_3$ induced ring slippage catalyses CO insertion into a methyl rhenium compound to produce an acetyl rhenium compound.[181] This reaction is remarkable in two respects: (1) the overall reaction is an apparent insertion of CO into an alkyl metal bond from outside the coordination sphere, and (2) the reaction involves a step in which the weak nucleophile CO induces an η^3- to η^1-cyclopentadienyl ring slippage.



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