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Reactions of Heterobimetallic Dihydrides. Our detailed investigations of the mechanism of the hydrogenation of alkynes by the heterobimetallic compound $\text{C}_5\text{H}_5(\text{CO})_2\text{Re}(\mu\text{-H})\text{Pt}(\text{H})(\text{PPh}_3)_2$ which produces rhenium alkene complexes, have led to several interesting discoveries. A summary of our progress in these investigations is in press.¹⁹³

The initial reaction of $\text{C}_5\text{H}_5(\text{CO})_2\text{Re}(\mu\text{-H})\text{Pt}(\text{H})(\text{PPh}_3)_2$ with alkynes produced *trans*- $\text{C}_5\text{H}_5(\text{CO})_2\text{ReH}_2$ and $(\text{alkyne})\text{Pt}(\text{PPh}_3)_2$. A least motion pathway should have produced *cis*- $\text{C}_5\text{H}_5(\text{CO})_2\text{ReH}_2$ initially. We have now found that *cis*- $\text{C}_5\text{H}_5(\text{CO})_2\text{ReH}_2$ can be produced by protonation of $\text{C}_5\text{H}_5\text{Re}(\text{CO})_2\text{H}^-$ at low temperature and that *cis*- $\text{C}_5\text{H}_5(\text{CO})_2\text{ReH}_2$ rapidly rearranges to *trans*- $\text{C}_5\text{H}_5(\text{CO})_2\text{ReH}_2$ at room temperature. *cis*- $\text{C}_5\text{H}_5(\text{CO})_2\text{ReH}_2$ was also observed as the initial product in the low temperature reaction of $\text{C}_5\text{H}_5(\text{CO})_2\text{Re}(\mu\text{-H})\text{Pt}(\text{H})(\text{PPh}_3)_2$ with alkynes.¹⁸⁹

Kinetic investigations of the reaction of $\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-H})\text{Pt}(\text{H})(\text{PPh}_3)_2$ 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 $\text{Cp}(\text{CO})_2\text{ReH}_2$ and

$\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-H})\text{Pt}(\text{H})(\text{PPh}_3)_2$, and rate determining unimolecular conversion of $\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-H})\text{Pt}(\text{H})(\text{PPh}_3)_2$ to a reactive intermediate committed to alkene complex formation. Higher concentrations of alkyne deplete the concentration of $\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-H})\text{Pt}(\text{H})(\text{PPh}_3)_2$ by shifting the equilibrium towards $\text{Cp}(\text{CO})_2\text{ReH}_2$ and $(\text{CH}_3\text{C}\equiv\text{CH})\text{Pt}(\text{PPh}_3)_2$; this lowers the concentration of $\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-H})\text{Pt}(\text{H})(\text{PPh}_3)_2$ and results in slower rates. The leading candidate for the reactive intermediate formed in the rate determining step is $\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-H})\text{Pt}(\text{H})(\text{PPh}_3)$, formed by unimolecular dissociation of PPh_3 from $\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-H})\text{Pt}(\text{H})(\text{PPh}_3)_2$.

Rate determining formation of the reactive intermediate $\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-H})\text{Pt}(\text{H})(\text{PPh}_3)$ by PPh_3 dissociation makes the risky prediction that the rates of alkyne reduction and phosphine exchange will be closely correlated. Every time $\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-H})\text{Pt}(\text{H})(\text{PPh}_3)$ 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*- $\text{Cp}(\text{CO})_2\text{ReH}_2$ with $\text{PhC}\equiv\text{CPh}$ catalyzed by a mixture of the two symmetrically labeled alkyne platinum complexes, $(\text{PhC}\equiv\text{CPh})\text{Pt}(\text{PPh}_3)_2$

and $(\text{PhC}\equiv\text{CPh})\text{Pt}(\text{PTol}_3)_2$. 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 $\text{PhC}\equiv\text{CPh}$ 4.3 times faster than the PPh_3 complex.

During the first 20 % conversion of $\text{PhC}\equiv\text{CPh}$ (0.13 M) and $\text{Cp}(\text{CO})_2\text{ReH}_2$ (0.13 M) to $\text{Cp}(\text{CO})_2\text{Re}(\text{PhHC}=\text{CHPh})$ catalyzed by a mixture of $(\text{PhC}\equiv\text{CPh})\text{Pt}(\text{PPh}_3)_2$ (0.031 M) and $(\text{PhC}\equiv\text{CPh})\text{Pt}(\text{PTol}_3)_2$ (0.023 M), the relative rate of hydrogenation to give $\text{Cp}(\text{CO})_2\text{Re}(\text{PhHC}=\text{CHPh})$ and of formation of mixed phosphine complex $(\text{PhC}\equiv\text{CPh})\text{Pt}(\text{PPh}_3)(\text{PTol}_3)$ 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 $\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-H})\text{Pt}(\text{H})(\text{PPh}_3)_2$.

In the course of preparing compounds related to intermediates in the reduction of alkynes with $\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-H})\text{Pt}(\text{H})(\text{PPh}_3)_2$, we studied the reaction of $\text{Cp}(\text{CO})_2\text{ReCH}_3\text{-Li}^+\cdot\text{THF}$ with *trans*- $(\text{PPh}_3)_2\text{Pt}[\text{C}(\text{CH}_3)=\text{CH}_2](\text{O}_3\text{SCF}_3)$ in an attempt to prepare $\text{Cp}(\text{CO})_2(\text{CH}_3)\text{RePt}[\text{C}(\text{CH}_3)=\text{CH}_2](\text{PPh}_3)_2$, but instead, we obtained $\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-CH}_2)\text{Pt}(\text{PPh}_3)_2$.¹⁸⁴ To account for the formation of $\text{Cp}(\text{CO})_2\text{Re}(\mu\text{-CH}_2)\text{Pt}(\text{PPh}_3)_2$, we propose that initial formation of intermediate $\text{Cp}(\text{CO})_2(\text{CH}_3)\text{RePt}[\text{C}(\text{CH}_3)=\text{CH}_2](\text{PPh}_3)_2$ 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.

Metal-Metal Double Bonds. We synthesized the unusual compound $\text{C}_5\text{Me}_5(\text{CO})_2\text{Re}=\text{Re}(\text{CO})_2\text{C}_5\text{Me}_5$ in which two 16e d^6 fragments are joined by a

metal-metal bond supported only by semibridging carbonyl groups.¹⁸⁰ We have observed many interesting reactions of $\text{C}_5\text{Me}_5(\text{CO})_2\text{Re}=\text{Re}(\text{CO})_2\text{C}_5\text{Me}_5$ including reversible addition of H_2 and interesting reactions with alkynes.¹⁹¹

Reactions of alkynes with $\text{C}_5\text{Me}_5(\text{CO})_2\text{Re}=\text{Re}(\text{CO})_2\text{C}_5\text{Me}_5$ have proven to be particularly fascinating and diverse. $\text{MeC}\equiv\text{CMe}$ reacts with $\text{C}_5\text{Me}_5(\text{CO})_2\text{Re}=\text{Re}(\text{CO})_2\text{C}_5\text{Me}_5$ at low temperature to produce a 1:1 adduct with a bridging carbonyl that fragments at room temperature to produce an η^4 -alkyne complex. $\text{HC}\equiv\text{CH}$ reacts with $\text{C}_5\text{Me}_5(\text{CO})_2\text{Re}=\text{Re}(\text{CO})_2\text{C}_5\text{Me}_5$ to give a product in which acetylene has been inserted Re and a carbonyl ligand. $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ reacts with $\text{C}_5\text{Me}_5(\text{CO})_2\text{Re}=\text{Re}(\text{CO})_2\text{C}_5\text{Me}_5$ to produce a symmetric 1 : 1 adduct that rearranges under fluorescent light to a compound in which each alkyne π -face is coordinated to a $\text{C}_5\text{Me}_5(\text{CO})_2\text{Re}$ group.

$C_5Me_5Co=CoC_5Me_5$ is Actually $(C_5Me_5)_3Co_3(\mu_2-H)_3(\mu_3-H)$.

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], 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 $C_5H_5Co(\mu-H)_{0-4}CoC_5H_5$ (collaboration with Bruce Bursten) indicated that $C_5H_5Co=CoC_5H_5$ should be diamagnetic but that $C_5H_5Co(\mu-H)_3$ or $4CoC_5H_5$ 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 $(C_5Me_5)_3Co_3(\mu_2-H)_3(\mu_3-H)$; (2) the compound Schneider studied by X-ray crystallography is $(C_5Me_5)Co(\mu-H)_3Co(C_5Me_5)$ and has δ 29 and (3) both compounds react with CO to produce $C_5Me_5Co(CO)_2$ and H_2 .¹⁸⁷

Reactions of $(C_5Me_5)_3Co_3(\mu_2-H)_3(\mu_3-H)$. The 46 electron paramagnetic tricobalt cluster $(C_5Me_5)_3Co_3(\mu_2-H)_3(\mu_3-H)$ is very reactive and has an interesting chemistry that we have begun to explore. In establishing the structure of $(C_5Me_5)_3Co_3(\mu_2-H)_3(\mu_3-H)$, we found that it reacted with excess CO to release H_2 and produce $Cp^*Co(CO)_2$. The reaction of $Cp^*_3Co_3(\mu_2-H)_3(\mu_3-H)$ with only two equivalents of CO forms the biscarbonyl dihydride cluster $Cp^*_3Co_3(\mu_3-CO)(\mu_2-CO)(\mu-H)_2$.¹⁹⁴ Upon heating at 80 °C, $Cp^*_3Co_3(\mu_3-CO)(\mu_2-CO)(\mu-H)_2$ loses H_2 to form the paramagnetic compound $Cp^*_3Co_3(\mu_3-CO)_2$.

Because isocyanides are isoelectronic with CO, we expected the reaction of *tert*-butyl isocyanide with $(C_5Me_5)_3Co_3(\mu_2-H)_3(\mu_3-H)$ to parallel the reaction of CO. In contrast, a surprisingly facile insertion of the isocyanide into a cobalt-hydrogen bond of $(C_5Me_5)_3Co_3(\mu_2-H)_3(\mu_3-H)$ occurred to produce the 48 electron formimidoyl cluster $Cp^*_3Co_3(\mu-H)(\mu_3-\eta^2-HC=NMe_3)$.¹⁹⁴ At low temperature, an intermediate, the 48 electron bis(isocyanide) cluster $Cp^*_3Co_3(\mu_3-CNCMe_3)(\mu_2-CNCMe_3)(\mu-H)_2$, was observed.

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

The reaction of the paramagnetic tetrahydride cluster, $\text{Cp}^*_3\text{Co}_3(\mu_2\text{-H})_3(\mu_3\text{-H})$ with acetylene led ultimately to the formation of a bis ethynylidyne cluster $\text{Cp}^*_3\text{Co}_3(\mu_3\text{-CCH}_3)_2$.¹⁹⁵ Two intermediates were detected during the course of the reaction: the diamagnetic monoethynidyne trihydride and $\text{Cp}^*_3\text{Co}_3(\mu_2\text{-H})_3(\mu_3\text{-CCH}_3)$ and the paramagnetic monoethynidyne monohydride $\text{Cp}^*_3\text{Co}_3(\mu_3\text{-H})(\mu_3\text{-CCH}_3)$. These two intermediates are kinetic products but can be interconverted at higher temperatures.

Wide Bite Angle Phosphines in Hydroformylation. We have published a full paper that correlates high *n* : *i* regioselectivity in hydroformylation with wide natural bite angles of chelating ligands.¹⁷⁷ We have studied the

deuterioformylation of 1-hexene using wide bite angle phosphines and have determined that the observed high selectivity for straight chain aldehydes is due to kinetic formation of a primary alkyl rather than equilibration of rhodium primary and secondary alkyls prior to hydroformylation. We have also prepared and determined the solid state and solution structures of (chelate)Ir(CO)₂H 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.

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