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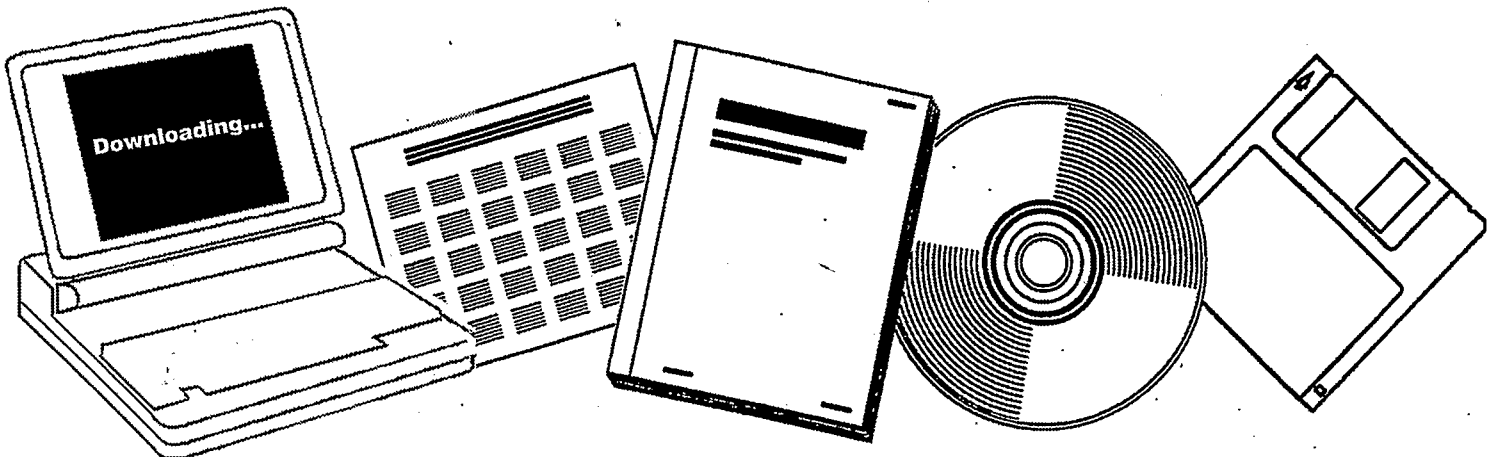
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**CATALYTIC HYDROGENATION OF CARBON
MONOXIDE. PROGRESS REPORT, DECEMBER 15,
1991--DECEMBER 14, 1992**

**PENNSYLVANIA UNIV., PHILADELPHIA. DEPT.
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CATALYTIC HYDROGENATION OF CARBON MONOXIDE

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Technical Report - Research Progress Report

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Project Title: Catalytic Hydrogenation of Carbon Monoxide

ABSTRACT

This project is focused on developing strategies to accomplish the reduction and hydrogenation of carbon monoxide to produce organic oxygenates at mild conditions. Our approaches to this issue are based on the recognition that rhodium macrocycles have unusually favorable thermodynamic values for producing a series of intermediates implicated in the catalytic hydrogenation of CO. Observations of metalloformyl complexes produced by reactions of H₂ and CO, and reductive coupling of CO to form metallo α -diketone species have suggested a multiplicity of routes to organic oxygenates that utilize these species as intermediates. Thermodynamic and kinetic-mechanistic studies are used in constructing energy profiles for a variety of potential pathways, and these schemes are used in guiding the design of new metallospecies to improve the thermodynamic and kinetic factors for individual steps in the overall process. Variation of the electronic and steric effects associated with the ligand arrays along with the influences of the reaction medium provide the chemical tools for tuning these factors. Emerging knowledge of the factors that contribute to M-H, M-C and M-O bond enthalpies is directing the search for ligand arrays that will expand the range of metal species that have favorable thermodynamic parameters to produce the primary intermediates for CO hydrogenation. Studies of rhodium complexes are being extended to non-macrocyclic ligand complexes that emulate the favorable thermodynamic features associated with rhodium macrocycles, but that also manifest improved reaction kinetics. Multifunctional catalyst systems designed to couple the ability of rhodium complexes to produce formyl and diketone intermediates with a second catalyst that hydrogenates these intermediates are promising approaches to accomplish CO hydrogenation at mild conditions.

Research Progress Report

Our research during the prior project period has been divided between developing a fundamental understanding of the CO reductive coupling process observed for rhodium(II) porphyrins and an attenuated continuing effort in exploring the formation and reactivity of metalloformyl species.

1) Porphyrin Ligands: Variation of Ligand Steric Requirements

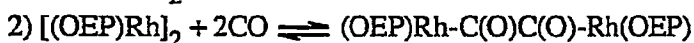
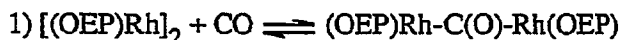
Systematic variation of porphyrin ligand steric demands has been used in tuning the effective M-M and M-C bond enthalpies which are important factors in determining the scope and thermodynamic selectivity in forming the organometallic species pertinent to this proposal. A list of porphyrin ligands arranged in the order of increasing steric demands is given below along with abbreviated names used throughout the proposal.

<u>porphyrin name</u>	<u>symbol</u>
Octaethylporphyrin	OEP
Tetraphenylporphyrin	TPP
Tetra(3,5-dimethylphenyl) porphyrin	TXP
Tetra(2,4,6-trimethylphenyl) porphyrin (Tetramesitylporphyrin)	TMP
Tetra(2,4,6-triethylphenyl) porphyrin	TTEPP
Tetra(2,4,6-triisopropylphenyl) porphyrin	TTiPP

Rhodium(II) and Iridium(II) porphyrin and related macrocycle complexes usually occur as metal-metal bonded dimers. When substituents with increasing steric demands are incorporated on the periphery of the porphyrin the interligand repulsions increase and the effective M-M bond dissociation enthalpy decreases ($D[(\text{OEP})\text{Rh}]_2 \sim 16 \text{ kcal mol}^{-1}$; $D[(\text{TXP})\text{Rh}]_2 \sim 12 \text{ kcal mol}^{-1}$; $D[(\text{OEP})\text{Ir}]_2 \sim 23 \text{ kcal mol}^{-1}$; $D[(\text{TXP})\text{Ir}]_2 \sim 19 \text{ kcal mol}^{-1}$). When the ligand steric demands are equal to or larger than that for tetramesityl porphyrin (TMP) the Rh(II) porphyrin complex is an $S=1/2$ paramagnetic monomer species, $(\text{por})\text{Rh}^\bullet$. EPR and NMR contact shifts have been used to demonstrate that the odd electron occupies the d_{z^2} in $(\text{por})\text{Rh}^\bullet$ species. $(\text{TTiPP})\text{Ir}^\bullet$ is the first example of a stable Ir(II) macrocycle. An interesting feature of this species is that the ^1H NMR contact shifts are compatible with the odd electron occupying the d_{xz} or d_{yz} orbital in contrast with the d_{z^2} occupancy observed for $(\text{por})\text{Rh}^\bullet$ species. The use of porphyrin ligand steric demands in tuning the effective M-C bond enthalpies is described in the proposal.

2) One-Electron CO Activation and CO Reductive Coupling

Activation of CO is typically accomplished by binding with Lewis acid metal centers which promote two electron reactions with nucleophiles at the carbonyl carbon.²⁴ We have recently illustrated an alternate approach to CO activation through the use of metalloradicals to induce one electron carbonyl reactions. This behavior was first realized in the reactions of octaethylporphyrinato rhodium(II) dimer, [(OEP)Rh]₂, with CO (equations 1, 2)¹³ that produce a dimetal ketone, (OEP)Rh-C(O)-Rh(OEP), which has precedent in the chemistry of Pd(I) and Pt(I) *A-frame* complexes,²⁵ and at higher CO pressures a dimetal α -diketone, (OEP)Rh-C(O)-C(O)-Rh(OEP), which was without precedent. Subsequent studies have shown that sequential increases

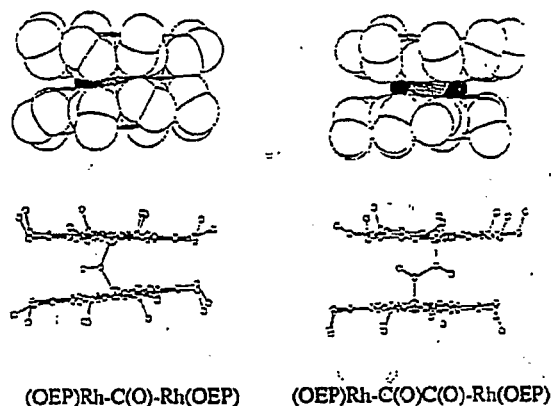


in porphyrin ligand steric requirements can be used to produce selectivity for CO reductive coupling (M-C(O)-C(O)-M) and that further increases in the ligand steric demands inhibit the CO coupling and permit direct observation of seventeen-electron mono CO complexes, [(por)Rh-CO].¹⁴⁻¹⁶ Kinetic and thermodynamic studies for the dimerization of the tetramesitylporphyrin derivative, (TMP)Rh-CO, to form (TMP)Rh-C(O)-C(O)-Rh(TMP) provide information on the nature of the 17-electron monocarbonyl and on the CO reductive coupling reaction. The monocarbonyls, [(por)Rh-CO], are found to have non-linear Rh-CO fragments and to react like acyl radicals in dimerizing through C-C bonding and in reactions with styrene and sources of hydrogen atoms.¹⁶

a) *Porphyrin Ligand Steric Effects on the Reactions of Rhodium(II) Porphyrins with CO:*

Rhodium(II) porphyrins are unusual in fulfilling the thermodynamic requirements to chemically reduce CO in forming dimetal ketone (M-C(O)-M) and dimetal α -diketone (M-C(O)-C(O)-M) complexes. Formation of a dimetal α -diketone in equilibrium with a dimetal ketone has particularly demanding thermodynamic criteria, because in addition to the need for relatively large absolute M-C bond energies (~ 47 kcal mol⁻¹), the effective M-C bond energy in the α -diketone must exceed that in the metalloketone by a minimum of 4-5 kcal mol⁻¹.¹³ This latter criterion is attainable by rhodium(II) porphyrin complexes because the bent single atom bridged metalloketone species are more sensitive to the steric demands of the porphyrin ligands than the two atom bridged M-C(O)-C(O)-M complexes where the two porphyrin rings are further apart and capable of attaining a near parallel orientation. Structure simulations given below for (OEP)Rh-C(O)-

Rh(OEP) and (OEP)Rh-C(O)C(O)Rh(OEP) illustrate the steric congestion in the dimetal ketone that is relieved in the dimetal diketone.

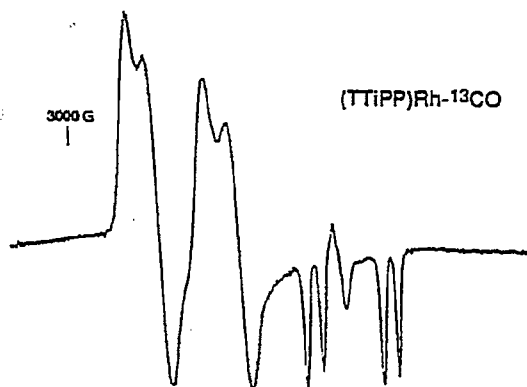


Steric effects are manifested in the equilibrium distribution of CO containing complexes observed for reactions of CO with a series of rhodium(II) porphyrin derivatives that have increasing steric demands (OEP < TXP < TMP < TTiPP). In the (OEP)Rh system the metalloketone is the majority species at all conditions studied ($P_{\text{CO}} = 0.1\text{-}30$ atm; $T = 220\text{-}300$ K) in the (TXP)Rh system it is a minority species observed only at low pressure ($P_{\text{CO}} < 0.4$ atm; $T = 298$ K) and metalloketone species are not observed at any conditions in reactions of CO with (TMP)Rh \cdot and (TTiPP)Rh \cdot . Decline in the thermodynamic stability of the metalloketone resulting from increased ligand steric demands in the (TXP)Rh and (TMP)Rh systems is accompanied by dramatic increases in the α -diketone species where at $P_{\text{CO}} = 1$ atm and $T = 298$ K greater than 99% of the rhodium porphyrin is incorporated into a CO reductive coupling product, (Rh-C(O)-C(O)-Rh). Increasing porphyrin ligand steric demands have thus been used to produce highly selective CO reductive coupling reactions. Further increase in the ligand steric demands associated with (TTEPP)Rh \cdot and (TTiPP)Rh \cdot produce interligand repulsions that inhibit the two-carbon bridged α -diketone species and result in observing only the paramagnetic ($S=1/2$) monocarbonyl complex [(TTiPP)RhCO] \cdot . A monocarbonyl complex, (Rh-CO) \cdot , is unobserved for (OEP)Rh and (TXP)Rh, a minority species with (TMP)Rh \cdot and the exclusive species for the (TTEPP)Rh \cdot and (TTiPP)Rh \cdot systems.

b) *One Electron Activation of CO*: Activation of CO by one electron steps is best known for radicals of the representative elements like methyl radicals which react with CO to form the transient acetyl radical ($\text{CH}_3\dot{\text{C}}\text{O}$).²⁶ The acetyl radical is an example of one electron activated CO

because it subsequently reacts by a second one electron reaction at the carbonyl carbon to produce acetone, $(\text{CH}_3)_2\text{CO}$, and biacetyl, $\text{CH}_3\text{-C(O)-C(O)-CH}_3$. In transition metal chemistry one electron activation of CO has been accomplished by reduction of 18-electron metal carbonyl complexes to form transient 19-electron species like $[(\text{CO})_4\text{Fe-CO}]^{\bullet-}$.²⁷ One important reaction of 19-electron carbonyl complexes is hydrogen atom abstraction from metal hydrides to form transient 18-electron metalloformyl species ($[(\text{CO})_4\text{Fe-CO}]^{\bullet-} + \text{H-M} \rightarrow (\text{CO})_4\text{Fe-C(O)H} + [\text{M}\cdot]$).²⁸ Comparable reactivity has also been observed for $[(\text{CO})_5\text{Cr-CO}]^{\bullet-}$, and other 19 electron metalcarbonyl complexes.²⁹

Reactions of sterically demanding $(\text{TMP})\text{Rh}\cdot$ and $(\text{TTiPP})\text{Rh}\cdot$ with CO have resulted in sufficient equilibrium concentrations of the 17-electron monocarbonyl species, $[(\text{TMP})\text{Rh-CO}]^\bullet$ and $[(\text{TTiPP})\text{Rh-CO}]^\bullet$, to permit direct observation by EPR and evaluation of the reactivity patterns for these species. Observation of three g values indicates that the d_{xz} and d_{yz} are non-degenerate which means that these complexes do not have a three fold or higher axis of symmetry. The removal of degeneracy of the d_{xz} , d_{yz} is ascribed to the presence of a non-linear Rh-CO unit which is predicted for the seven-electrons case ($d^7 + \pi^*0$) when the metal and diatomic molecule are capable of relatively strong covalent sigma bonding.³⁰ The bent M-CO units observed in $[(\text{por})\text{RhCO}]^\bullet$ complexes are preceded only by nineteen electron complexes like $[\text{Fe}(\text{CO})_5]^{\bullet-}$ where the odd electron is required to occupy a predominantly ligand (CO) based orbital. $(\text{por})\text{Rh-CO}$ complexes are at present the only examples where a bent M-CO unit is induced by effective M-CO σ bonding.



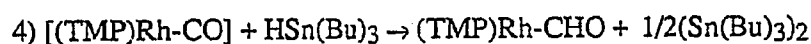
Frozen solution EPR spectra for $(\text{TTiPP})\text{Rh}^{13}\text{CO}$ in toluene glass (90 K) ($g_1 = 2.167$; $g_2 = 2.138$; $g_3 = 2.000$; $A(^{13}\text{C}_{(g1)}) = 318$ MHz; $A(^{13}\text{C}_{(g2)}) = 347$ MHz; $A(^{13}\text{C}_{(g3)}) = 305$ MHz; $A(^{13}\text{Rh}_{(g3)}) = 65$ MHz).

Reactions of $[(\text{TMP})\text{Rh-CO}]^\bullet$ illustrate that this complex mimics acyl radical reactions rather than metal centered radical reactivity. Reversible dimerization of $[(\text{TMP})\text{Rh-CO}]^\bullet$ through C-C bond formation to produce a 1,2 ethanedionyl complex, $(\text{TMP})\text{Rh-C(O)-C(O)-Rh}(\text{TMP})$

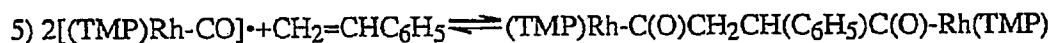
(equation 3) illustrates a carbonyl carbon centered one electron reaction that can be viewed as an organometallic analog of acyl radical coupling ($2\dot{\text{R}}\text{CO} \rightarrow \text{R-C(O)C(O)-R}$).



Reaction of $[(\text{TMP})\text{Rh-CO}] \cdot$ with $(\text{Bu})_3\text{Sn-H}$ to form $(\text{TMP})\text{Rh-CHO}$ provides an illustration of a metal hydride transferring a hydrogen atom to the carbonyl carbon rather than to the Rh(II) center (equation 4). Alkenes are known to react rapidly with rhodium(II) porphyrins by radical like



processes to form alkyl bridged complexes $(\text{por})\text{Rh-CH}_2\text{-CH(X)-Rh}(\text{por})$. The reaction of styrene with $[(\text{TMP})\text{Rh-CO}] \cdot$ provides another opportunity to examine whether the Rh(II) metal based radical ($\cdot\text{Rh:C}\equiv\text{O}$) or acyl radical ($\text{Rh}-\dot{\text{C}}\equiv\text{O}$) nature is manifested. When the equilibrium distribution of $(\text{TMP})\text{Rh-C(O)-C(O)-Rh}(\text{TMP})$ and $[(\text{TMP})\text{Rh-CO}] \cdot$ is preformed at CO pressures where virtually all of the $(\text{TMP})\text{Rh}\cdot$ is reacted ($P_{\text{CO}} > 0.3\text{atm}$), subsequent reaction with styrene forms $(\text{TMP})\text{Rh-C(O)CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{C(O)-Rh}(\text{TMP})$ as the only observed species in the $^1\text{H NMR}$ (equation 5).

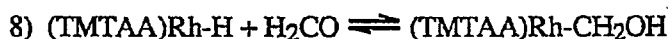
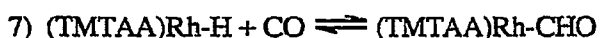
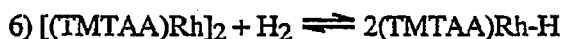


Presumably $[(\text{TMP})\text{Rh-CO}] \cdot$ interacts with styrene to form an intermediate of the form $[(\text{TMP})\text{Rh-C(O)CH}_2\text{CH}(\text{C}_6\text{H}_5)] \cdot$ which is trapped by a second $[(\text{TMP})\text{Rh-CO}]$. The styrene reaction is further evidence that $[(\text{TMP})\text{Rh-CO}] \cdot$ has a strong preference to function like an acyl rather than a metal based radical.

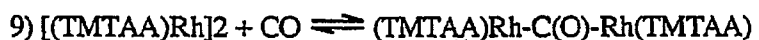
The electronic structures of $[(\text{por})\text{Rh-CO}] \cdot$ species are between the limiting electron structures that localize the odd electron either in the rhodium d_{z^2} ($\cdot\text{Rh:C}\equiv\text{O}$) or on the carbonyl carbon ($\text{Rh}-\dot{\text{C}}\equiv\text{O}$). Results from EPR studies indicate that the odd electron spin density on CO is ~ 0.3 . The 17-electron carbonyl complex, $(\text{TMP})\text{RhCO}$, is thus poised for a second one-electron reaction at either the rhodium or carbonyl carbon sites. Reaction of $[(\text{TMP})\text{Rh-CO}] \cdot$ with a 1-electron species $\text{X}\cdot$ at the metal would produce an 18-electron Rh(III) carbon monoxide complex, $(\text{TMP})\text{Rh}(\text{X})(\text{CO})$, while reaction at the carbonyl carbon would form a 16-electron Rh(III) complex, $(\text{TMP})\text{RhC(O)X}$. All of the one-electron radical-like reactions of $(\text{TMP})\text{RhCO}$ that have been observed occur at the carbonyl carbon to form 16-electron rhodium(III) complexes. To our knowledge, this reactivity pattern of $[(\text{TMP})\text{Rh-CO}] \cdot$ is currently unique among 17-electron metal carbonyls.

3) Reactions of (TMTAA)Rh Complexes with H₂, CO and H₂CO

The rhodium (II) complex of dibenzotetramethyltetraaza [14] annulene (TMTAA) occurs as a Rh-Rh bonded dimer, [(TMTAA)Rh]₂. [(TMTAA)Rh]₂ reacts with H₂ to form a hydride complex, (TMTAA)Rh-H, which subsequently reacts with CO and aldehydes to form metalloformyl, (TMTAA)Rh-CHO, and α-hydroxyalkyl complexes, (TMTAA)Rh-CH(R)OH (equations 6-8). [(TMTAA)Rh]₂ also reacts with CO to form a dimetalketone



(TMTAA)Rh-C(O)-Rh(TMTAA) (equation 9), but does not form a dimetal α-diketone complex (M-C(O)C(O)-M) in observable concentrations at up to 30 atmospheres pressure of CO. TMTAA



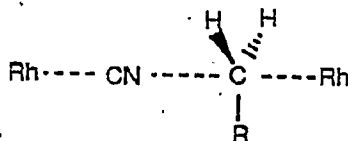
has smaller steric demands than porphyrins, and this observation supports our model that substantial formation of a dimetal α-diketone depends on relief of steric effects in the dimetal ketone. The dianion of (TMTAA) is antiaromatic 16 pi electron ligand. The similarity of the reactivity of the Rh(II) and Rh-H derivatives with rhodium porphyrins illustrates that the aromatic pi electron structure of porphyrins is not an essential feature for the unusual M-H and M-C bond enthalpies associated with rhodium porphyrins. This is an important result for our continuing studies because it suggests that many related ligand arrays may yield rhodium complexes with the appropriate thermodynamic parameters needed to produce formyl complexes from reaction with H₂ and CO.

4) Reactions of isocyanides with (por)Rh(II) and (por)Rh-H complexes

Isocyanides have similar electron structures and reactivity patterns but generally enhanced reactivity when compared to carbon monoxide and are used to model and define the range of potential carbon monoxide reactivity. The reactions of carbon monoxide with (por)Rh(II) complexes give a 1:1 CO adduct, a dimetallo ketone and a dimetallo diketone in an equilibrium distribution. Alkyl isocyanides react with (por)Rh(II) species to form 1:1 complexes and subsequent N-R bond cleavage to yield (por)Rh-CN and (por)Rh-R complexes in equal quantities as the exclusive products (R = Me, n-Bu). The reaction occurs in the time of mixing for (TMP)Rh• and proceeds in a few hours with [(OEP)Rh]₂ which suggests the importance of metalloradicals in the process. No evidence was found for bridging isocyanide complexes that

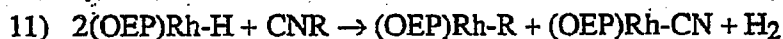
would be analogous to the dimetal ketone and dimetal α -diketone species observed for CO reactions with (por)Rh^{II} species undoubtedly due to steric effects of the isocyanide alkyl group.

The N-R bond breaking probably occurs by a radical process where the isocyanide coordinates to (por)Rh[•] which is attacked by a second metalloradical to form Rh-CN and Rh-R bonds in a concerted step. The proposed transition state is similar to that suggested for the

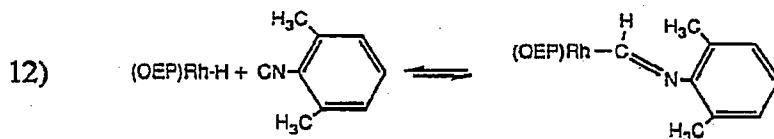


activation of methane by (TMP)Rh[•].

(OEP)Rh-H was anticipated to react with isocyanides to yield metalloformimidoyl complex in analogy with the CO reaction that forms (OEP)Rh-CHO (equation 10). Methyl isocyanide and n-butyl isocyanide do yield the corresponding formimidoyl compounds but the system reacts further to produce the alkyl and cyanide complexes associated with CN-R bond cleavage (equation 11). Using the sterically hindered and rigid 2,6-xylyl isocyanide results in exclusive



formation of the metalloformimidoyl species without N-R bond cleavage products (equation 12).

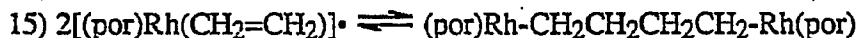
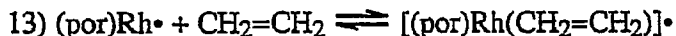


Addition of acid to the formimidoyl complex results in a significant downfield shift of the porphyrin methyne hydrogen resonance indicating the formation of a cationic type compound, tentatively assigned to the Fischer carbene complex $[(\text{OEP})\text{Rh}=\text{CH}(\text{NHR})]^+$. Related protonations of formyl complexes are currently being evaluated.

5) Metalloradical Reactions of Ethene

Transition metal bonding and activation of alkenes by two electron processes occupies a prominent position in organometallic catalysis chemistry,³² but the potential of one-electron metalloradical reactions with alkenes remains relatively underdeveloped. A series of rhodium(II) porphyrin ($d^7, s = 1/2$) complexes where the ligand steric demands are incrementally increased has been used in studying metalloradical reactions of ethene. Tetramesitylporphyrinato rhodium(II), (TMP)Rh•, and complexes with smaller ligand steric requirements react with ethene to form two-carbon alkyl bridged complexes, (por)Rh-CH₂CH₂-Rh(por). Increasing the porphyrin steric demands by replacing the methyl substituents of TMP with ethyl and isopropyl groups results in rhodium(II) complexes that produce ethene coupling (M-CH₂CH₂CH₂CH₂-M), and permit observation of an intermediate metalloradical-ethene complex, [(por)Rh(CH₂=CH₂)]•. EPR studies demonstrate that the intermediate contains an ethene that is bonded in an η^2 mode and further provides an unusually detailed experimental view of the interaction between an alkene and a metal center.

Alkene reactions of Rh(II) porphyrins that produce alkyl bridged complexes can be envisioned as occurring through the intermediacy of a metalloradical-alkene complex (equations 13-15). Interaction of a radical (X•) with ethene to form substantial concentrations of an alkyl radical (X-CH₂CH₂•) requires an X-CH₂ bond dissociation enthalpy of approximately 72 kcal mol⁻¹.

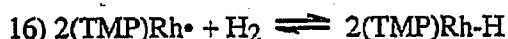


Metalloradical reactions of (por)Rh• species with alkenes differ from alkyl radical reactions in that the (por)Rh-CH₂ bond dissociation enthalpy (~50 kcal mol⁻¹) is insufficient to justify formation of an authentic carbon-based alkyl radical intermediate ((por)Rh-CH₂CH₂•). Concerted formation of two Rh-CH₂ bonds is required for alkene reduction and this feature provides the opportunity to achieve selectivity for metalloradical reactions. The large steric demands of (TTEPP)Rh prohibit formation of a two-carbon bridged complex and the reaction proceeds to give a four-carbon alkene coupling product ((por)Rh-(CH₂)₄-Rh(por)) which relieves the steric congestion. Alkene oligomerization stops at the dimer because further radical reaction requires homolysis of a relatively strong Rh-CH₂- bond. We are currently evaluating reactions for a wide variety of metalloradicals and alkenes in an effort to determine the generality and efficacy for this type of controlled radical process.

6) Metalloradical Reactions with H₂ and D₂

Metal catalyzed hydrogenation of substrates involves addition of hydrogen to the metal center as an obligatory step.³³ The importance of this class of reactions has stimulated efforts to understand the scope of mechanistic pathways operative in reactions of H₂ with metal complexes. As part of our program to evaluate the metalloradical reactions of rhodium(II) macrocycles with substrates like CH₄, CO, CH₂=CH₂, we have studied the reactions of (TMP)Rh• with H₂ and D₂.³⁴

Benzene solutions of (TMP)Rh• (~5 x 10⁻⁴M) react with H₂ (P_{H₂} = 0.2 ~1.0 atm.) to form the hydride complex, (TMP)Rh-H (equation 16). Reaction 16 is well suited for kinetic studies



because it is free from any competitive processes such as solvent reactions, M-M bond formation, and hydrogenation of the ligand, which have complicated previous studies of H₂ reactions with metalloradicals. The rate for reaction 16 is observed to have a second-order dependence on the molar concentration of (TMP)Rh• first-order rate dependence on the molar concentration of H₂ and an overall third order rate law for reaction 16 (rate₍₁₆₎ = k₁₆[(TMP)Rh•]²[H₂]). Temperature dependence of the third order rate constant (k₁₆) was used in deriving estimates for the transition state and Arrhenius activation parameters (ΔH_{(16)‡}(H₂) = 4.9 kcal mol⁻¹, ΔS_{(16)‡}(H₂) = -40 cal K⁻¹ mol⁻¹; A(H₂) = 2.9 x 10⁴, ΔE_{(16)‡}(H₂) = 5.5 kcal mol⁻¹). Parallel studies for the reaction of D₂ with (TMP)Rh• provide the kinetic isotope effect on the rate (k_(H₂)/k_(D₂)(296K) = 1.6; k_(H₂)/k_(D₂)(353K) = 1.3) and activation parameters (ΔH_{(16)‡}(D₂) = 5.5 kcal mol⁻¹, ΔS_{(16)‡}(D₂) = -39 cal K⁻¹ mol⁻¹; A(D₂) = 5.0 x 10⁴, ΔE_{(16)‡}(D₂) = 6.1 kcal mol⁻¹).

The rate law for reaction 16, (rate₍₁₆₎ = k₁₆[(TMP)Rh•]²[H₂]) establishes that the transition state contains two (TMP)Rh• metalloradicals and H₂. A large negative activation entropy (ΔS_{(16)‡} = -40 cal K⁻¹ mol⁻¹) and small activation enthalpy (ΔH_{(16)‡} = 4.9 kcal mol⁻¹) are also consistent with organizing three molecules into a transition state (TS) where evolution of two Rh-H bonds substantially compensates for the H-H bond breaking. Transition states of this general type have been previously implicated in reactions of dihydrogen with iodine atoms³⁵ and cobalt(II) metalloradicals.³⁶



We have also recently invoked this type of TS for the reaction of methane with (TMP)Rh• (Rh••CH₃••H••Rh) on the basis of the rate law (rate_f = k_f[(TMP)Rh•]²[CH₄]), activation parameters (ΔS[‡] = -39 cal K⁻¹ mol⁻¹; ΔH[‡] = 7.1 kcal mol⁻¹), and the kinetic isotope effect (k(CH₄)/k(CD₄) (296 K) = 8.2).³⁷

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• Publications associated with DOE-FG02-86ER13615

"Organometallic Reactions of Rhodium Octaethylporphyrin Species in Pyridine: Heterolytic Cleavage of [(OEP)Rh]₂ and Metallo Anion Activation of CO," B.B. Wayland, K.J. Balkus, and M.D. Farnos, *Organometallics*, 1989, 8, 950.

"Thermodynamics for the Addition of [(OEP)Rh]₂ with Propene and Observation of a Facile Dyotropic 1,2 Exchange of (OEP)Rh Groups in (OEP)Rh-CH₂CH(CH₃)-Rh(OEP)," B.B. Wayland, Y. Feng and S. Ba, *Organometallics*, 1989, 8, 1438.

"Metalloradical Activation of CO: Formation and Carbonyl Coupling of a Bent 17-Electron M-CO Unit," A.E. Sherry and B.B. Wayland, *J. Am. Chem. Soc.* 1989, 111, 5010.

"Selective Reductive Coupling of Carbon Monoxide," B.B. Wayland, V.L. Coffin and A.E. Sherry, *J. Chem. Soc. Chem. Commun.* 1989, 662.

"Thermodynamic Studies of the Hydrogenation and Reductive Coupling of Carbon Monoxide by Rhodium(II) Porphyrins," B.B. Wayland, V.L. Coffin, A.E. Sherry, and W.R. Brennen, in "Bonding Energetics in Organometallic Compounds," T.J. Marks, Ed. ACS Symposium Series No. 428, American Chemical Society: Washington, D.C. 1990, pp. 148-158.

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