

Factors contributing to one-electron metalloradical activation of ethene and carbon monoxide illustrated by reactions of Co(II), Rh(II), and Ir(II) porphyrins

Weihong Cui, Shan Li, Bradford B. Wayland *

Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, United States

Received 14 December 2006; received in revised form 10 January 2007; accepted 11 January 2007

Available online 20 January 2007

Abstract

Metallo-porphyrin complexes of Co(II), Rh(II), and Ir(II) are used as prototype metal-centered radicals in examining the factors that contribute to obtaining one-electron activated ethene and CO substrate adducts $[M(\text{CH}_2\text{CH}_2)]^\ddagger$ and $[M(\text{CO})]^\ddagger$ that subsequently react on to produce complexes with reduced substrate units including $M\text{-CH}_2\text{CH}_2\text{-M}$, $M\text{-(CH}_2)_4\text{-M}$, $M\text{-C(O)-M}$, $M\text{-C(O)-C(O)-M}$, and $M\text{-C(O)H}$. Cobalt(II) and rhodium(II) complexes of the form $[(\text{por})M(\text{CH}_2\text{CH}_2)]^\ddagger$ and $[(\text{por})M(\text{CO})]^\ddagger$ occur as primarily metal-centered radicals and the iridium analogs are porphyrin anion radical complexes $(\text{por})^-\text{Ir}^{\text{III}}(\text{CH}_2\text{CH}_2)$, $(\text{por})^-\text{Ir}^{\text{III}}(\text{CO})$. Relatively small (por)Co–C bond dissociation enthalpies preclude forming any reduced substrate species. Rhodium porphyrins produce a complete set of reduced and coupled ethene and CO complexes, but iridium porphyrins only give ethene reduction and coupling products (por)Ir–CH₂CH₂–Ir(por) and (por)Ir–(CH₂)₄–Ir(por). Thermodynamic criteria and analysis of substrate reactions are used to guide interpretations of the observed reactivity.

© 2007 Elsevier B.V. All rights reserved.

Keywords: One-electron activation; Group nine metallo-porphyrins; Ethene and CO reduction and coupling; Organo-metal thermodynamics

1. Introduction

Reactions of metal-centered radicals are attracting attention as potential pathways to attain new classes of organometallic substrate transformations [1–12] and catalytic processes [13–18]. One of the initial motivations for our interest in metal-centered radicals (M^\cdot) was to explore the potential for metallo-radicals to induce one-electron carbon-centered reactions of substrates like ethene and CO in analogy with reactions of hydrogen atom (H^\cdot) and methyl radical (CH_3^\cdot). Formation and reactions of paramagnetic alkene complexes of rhodium and iridium are the subject of a recent microreview that is highly relevant to this area [19]. Organometallic reactivity of carbon monoxide is experiencing resurgent interest resulting from the recognition that CO from synthesis gas is the probable

future carbon source for organic molecules to replace petroleum [20,21]. This renewed focus on CO activation and transformation has stimulated reopening the evaluation of one-electron metallo-radical reactions with CO as a potential approach to obtain unusual types of reactions such as carbon monoxide reductive coupling [20].

This article examines the factors that contribute to metal-centered radicals accomplishing one-electron activation of ethene and CO by forming $[M(\text{CH}_2\text{CH}_2)]^\ddagger$ and $[M(\text{CO})]^\ddagger$ species that subsequently react on to produce complexes with reduced substrate units including $M\text{-CH}_2\text{CH}_2\text{-M}$, $M\text{-(CH}_2)_4\text{-M}$, $M\text{-C(O)-M}$, $M\text{-C(O)-C(O)-M}$, and $M\text{-C(O)H}$. Group nine (Co(II), Rh(II), Ir(II)) (d^7) metallo-porphyrin complexes are used as prototype metal-centered radicals to examine these factors that contribute to obtaining substrate reduction. A recurring theme in this study is the use of ligand steric demands that vary from octaethylporphyrin (OEP) to tetra(2,4,6-triisopropylphenyl) porphyrin (TTiPP) to assist in directing the

* Corresponding author. Tel.: +1 215 898 8633; fax: +1 215 573 6743.
E-mail address: wayland@sas.upenn.edu (B.B. Wayland).

metallo-radical substrate reactions [22–25]. The structures and abbreviated names for all of the porphyrins used in this article are shown in Fig. 1. Composite results from reactivity studies and thermodynamic measurements on a series of porphyrin group nine metallo-radical systems are used in an effort to identify the factors that define the range of ethene and CO substrate reactions that result in forming complexes with reduced substrate units.

2. Results and discussion

2.1. Cobalt(II), rhodium(II), and iridium(II) porphyrins as metal-centered radicals

Cobalt(II) porphyrins are invariably monomeric ($S = 1/2$) species [26,27], but rhodium(II) and iridium(II) derivatives with lower steric requirement porphyrins, such as octaethylporphyrin (OEP) and tetraphenylporphyrin (TPP), occur as metal–metal bonded dimers [28,29]. Inter-porphyrin repulsions not only prohibit the cobalt(II) centers from reaching an effective $\text{Co}^{\text{II}}\text{--Co}^{\text{II}}$ bonding distance, but also reduce the $\text{Rh}^{\text{II}}\text{--Rh}^{\text{II}}$ and $\text{Ir}^{\text{II}}\text{--Ir}^{\text{II}}$ bond dissociation enthalpies such that the $\text{M}\text{--M}$ bonded dimers are facile sources of metal-centered radicals ($(\text{por})\text{Rh}^{\text{II}}$, $(\text{por})\text{Ir}^{\text{II}}$). Temperature dependence of the ^1H NMR line broadening [30,31] has been applied as an approach to determine the activation parameters for homolysis of the $\text{Ir}\text{--Ir}$ bond in $(\text{OEP})\text{Ir}\text{--Ir}(\text{OEP})$ (Fig. 2). The measured activation enthalpy for the $\text{Ir}^{\text{II}}\text{--Ir}^{\text{II}}$ homolysis ($\Delta H^\ddagger = 26 \text{ kcal mol}^{-1}$) provides an estimate of $\sim 24 \text{ kcal mol}^{-1}$ for the $(\text{OEP})\text{Ir}\text{--Ir}(\text{OEP})$ bond dissociation enthalpy (BDE). The corresponding activation enthalpy for $(\text{OEP})\text{Rh}\text{--Rh}(\text{OEP})$ bond homolysis ($\Delta H^\ddagger = 18.5 \text{ kcal mol}^{-1}$) and $\text{Rh}^{\text{II}}\text{--Rh}^{\text{II}}$ BDE ($\Delta H^\circ \sim 16 \text{ kcal mol}^{-1}$) [30] that were also determined by ^1H NMR line broadening are about 8 kcal mol^{-1} less than the values for the iridium(II) porphyrin derivatives. Increasing the porphyrin steric demands to that of tetramesitylporphyrin (TMP), tetra(2,4,6-triethylphenyl) porphyrin (TTEPP), and tetra(2,4,6-triisopropylphenyl) porphyrin (TTiPP) produces stable rhodium(II) [22,24] and iridium(II) [25] metal-centered radicals $(\text{TMP})\text{M}^{\text{II}}$, $(\text{TTEPP})\text{M}^{\text{II}}$, and $(\text{TTiPP})\text{M}^{\text{II}}$ ($\text{M} = \text{Rh}, \text{Ir}$).

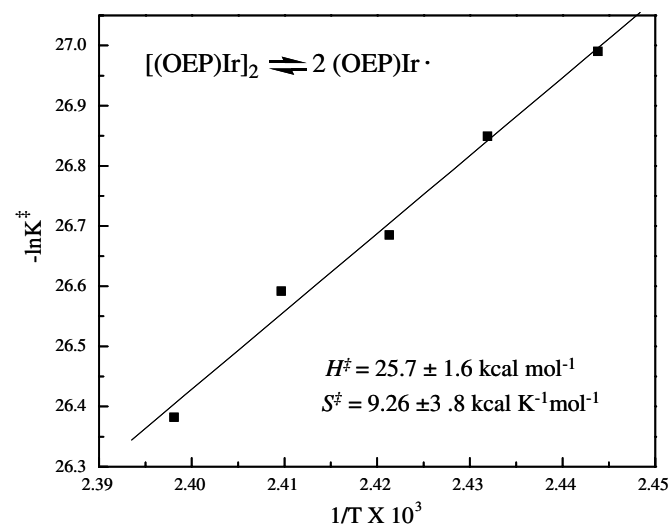


Fig. 2. Determination of the activation energy for dissociation of the $\text{Ir}\text{--Ir}$ bond of $[(\text{OEP})\text{Ir}]_2$ in benzene- d_6 by ^1H NMR line broadening.

rhodium(II) [22,24] and iridium(II) [25] metal-centered radicals $(\text{TMP})\text{M}^{\text{II}}$, $(\text{TTEPP})\text{M}^{\text{II}}$, and $(\text{TTiPP})\text{M}^{\text{II}}$ ($\text{M} = \text{Rh}, \text{Ir}$).

EPR studies [27] and relative high level computations [32] show that cobalt(II) porphyrins have an $^2\text{A}_{1g}$ ground state from the $(d_{xy})^2(d_{xz,yz})^4(d_{z^2})^1$ configuration which is separated from $^2\text{E}_g$ excited state $((d_{xy})^2(d_{z^2})^2(d_{xz,yz})^3)$ by only $1000\text{--}2000 \text{ cm}^{-1}$. Rhodium(II) porphyrins also have the $^2\text{A}_{1g}$ ground state and the $^2\text{E}_g$ excited state with an $^2\text{E}_g \leftarrow ^2\text{A}_{1g}$ separation of $\sim 9800 \text{ cm}^{-1}$ [33], which is substantially larger than that for the cobalt(II) derivative. Lowering of the filled $d_{xz,yz}$ by intermixing with the porphyrin π contributes to placing the $d_{xz,yz}$ below d_{z^2} . Previous studies showed that the iridium(II) porphyrin metallo-radical $(\text{TTiPP})\text{Ir}^{\text{II}}$ surprisingly has an $^2\text{E}_g$ ground state $(d_{xy})^2(d_{z^2})^2(d_{xz,yz})^3$ electron configuration with a close lying $^2\text{A}_{1g}$ excited state [25].

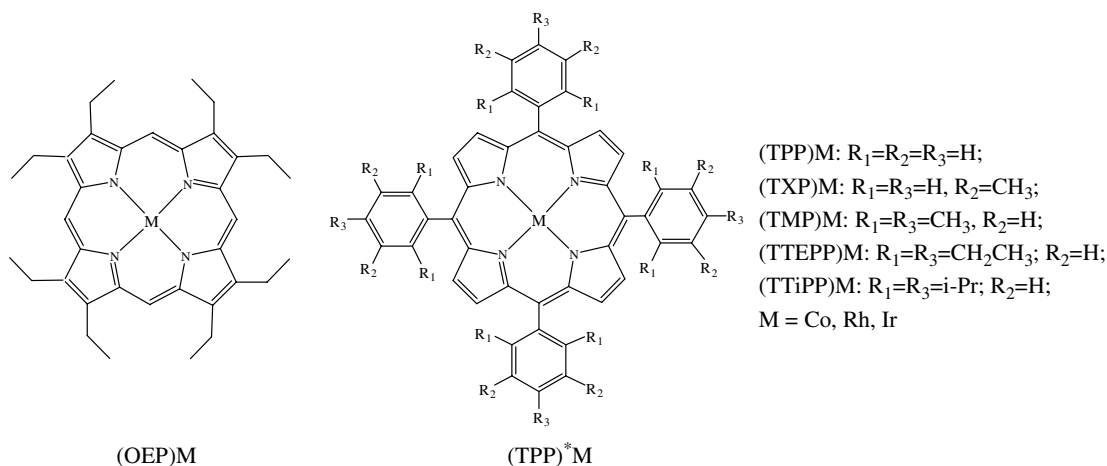


Fig. 1. Illustration of porphyrin metal complexes with different steric demands.

2.2. Donor adducts of (por) M^{II} ($M = \text{Co}, \text{Rh}, \text{Ir}$)

Interaction of the group nine metal-centered radicals with donor molecules results in raising the energy of the d_{z^2} and increases the $d_{xz,yz}$ to d_{z^2} energy separation [33]. Cobalt(II) porphyrins react with donors such as pyridine to form mono donor (17-electron) and bis donor (19-electron) adducts that have clearly defined $(d_{xy})^2(d_{xz,yz})^4(d_{z^2})^1$ ground state configuration [33] (Fig. 3). (TMP)Rh^{II} forms a 1:1 complex with pyridine ((TMP)Rh(Py)) that has a $(d_{z^2})^1$ electron configuration, but when an additional pyridine binds to form the bis donor adduct (TMP)Rh(Py)₂, an intra-molecular electron transfer occurs to form a porphyrin anion radical complex of rhodium(III) (TMP)⁻Rh^{III}(Py)₂ [33] (Fig. 3). Efforts to observe (por)Ir^{II}-donor adducts have thus far only produced (por)⁻Ir^{III} complexes. The higher energy of the iridium 5d orbitals and larger interaction with axial donor ligands invariably raises the energy of the d_{z^2} antibonding orbital above the porphyrin LUMO π^* which results in the transfer of one electron from the iridium(II) metal center to the redox non-innocent porphyrin ligand π^* orbitals (Fig. 3). The LUMO (π^*) of the porphyrin ligand thus establishes an upper limit for the unpaired electron energy in the d_{z^2} orbital which indirectly influences the scope of metal-centered radical species.

Each of the group nine metallo-radicals ((por) M^{II}) reacts with CO to form a different type of CO complex. The cobalt(II) derivative exclusively forms 1:1 adducts (Co^{II}(CO)) which have axial symmetry determined by EPR at low temperatures [33]. Rhodium(II) derivatives form 1:1 17-electron mono-CO complexes ((por)Rh(CO)) which have non-linear Rh–C–O units shown by the non-axial g tensor observed in the EPR spectra [33] (Fig. 4). Iridium(II) porphyrins ((por)Ir^{II}) react with CO to form Ir(III) complexes (por)⁻Ir^{III}(CO) _{n} ($n = 1$ or 2) where EPR spectra show the presence of the porphyrin anion radical [34] (Fig. 4).

2.3. Reactions of ethene with (por) M^{II} ($M = \text{Co}, \text{Rh}, \text{Ir}$)

CO (OEP)Co^{II} does not interact with ethene to produce an observable perturbation on the ¹H NMR or electronic spectrum in benzene ($P_{\text{ethene}} \sim 1$ atm, $T = 298$ K). However, both the rhodium(II) and iridium(II) metal–metal

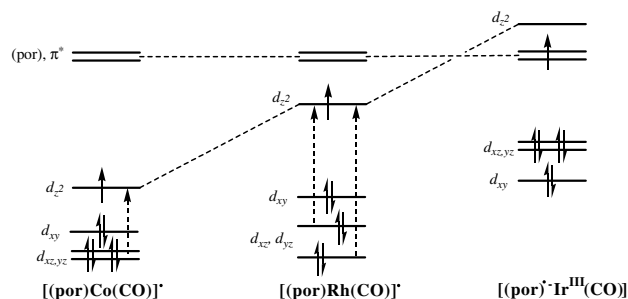
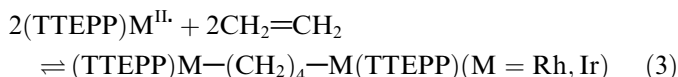
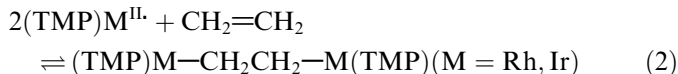
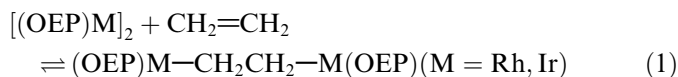


Fig. 4. Schematic MO diagram for [(por)M(CO)] ($M = \text{Co}^{\text{II}}, \text{Rh}^{\text{II}}, \text{Ir}^{\text{II}}$, $P_{\text{CO}} < 1$ atm)

bonded dimers of OEP complexes and monomeric TMP metallo-radical complexes react with ethene to form bridged ethylene complexes (Eqs. (1) and (2)). Increasing the porphyrin steric demands to that of TTEPP inhibits the formation of the two carbon atom bridged compound and both the rhodium(II) and iridium(II) derivatives manifest ethylene coupling to give four-carbon bridged complexes (Eq. (3)) [24]. Further increasing the porphyrin steric requirement to



TTiPP kinetically hinders formation of the four-carbon ethene coupling compounds which permits observation of a rhodium(II) ethene adduct [(TTiPP)Rh(CH₂=CH₂)]⁺ (Eq. (4)) (Fig. 5) [24]. Spectroscopic results for the ethene reaction with (TTiPP)Ir^{II} indicate that an iridium(III) porphyrin anion radical species (TTiPP)⁻Ir^{III}(CH₂=CH₂) forms as a result of a donor induced intra-molecular electron transfer from the metal to porphyrin π^* orbital (Eq. (5)) (Fig. 5) [25].

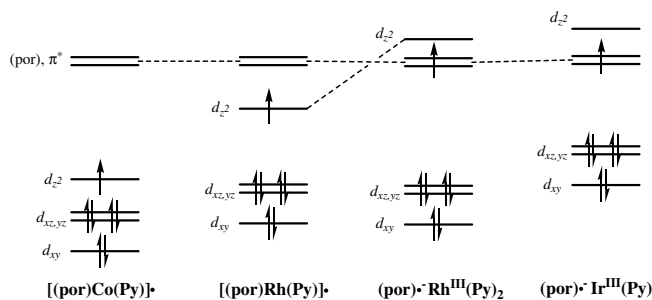
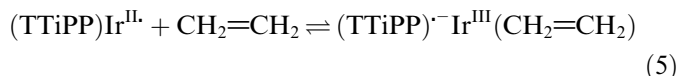
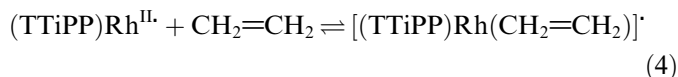


Fig. 3. Schematic MO diagram for (por)M(pyridine) ($M = \text{Co}^{\text{II}}, \text{Rh}^{\text{II}}, \text{Ir}^{\text{II}}$).

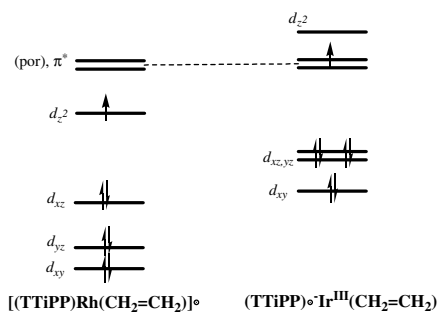
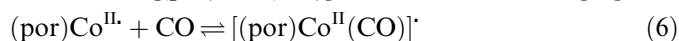


Fig. 5. Schematic MO diagram for [(TTiPP)M(CH₂=CH₂)]⁺ ($M = \text{Rh}^{\text{II}}, \text{Ir}^{\text{II}}$, $P_{\text{ethene}} \sim 1$ atm).

2.4. Reactions of CO with group nine metal porphyrin complexes

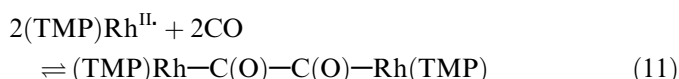
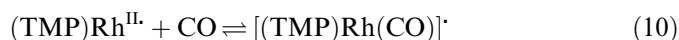
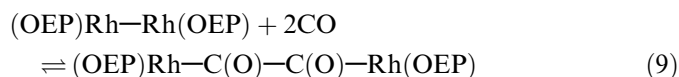
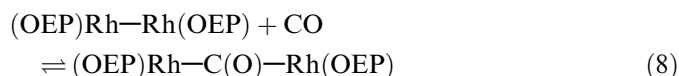
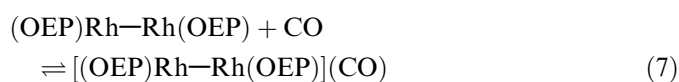
2.4.1. Reactions of (por)Co^{II} complexes with CO

Cobalt(II) porphyrins react with CO exclusively to form 1:1 complexes at low temperature (Eq. (6)) and no further reactions of [(por)Co^{II}(CO)][•] have been observed [33]

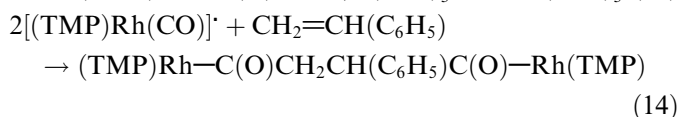
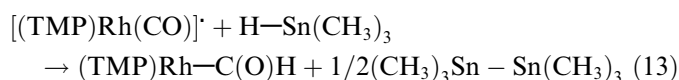


2.4.2. Reactions of (por)Rh^{II} complexes with CO

(OEP)Rh–Rh(OEP) reacts with CO at $P_{\text{CO}} \sim 1$ atm to give an equilibrium distribution of a CO adduct (Eq. (7)) with a diamagnetic metallo-ketone (Eq. (8)) and at higher CO pressures produces a dimetal diketone complex (Eq. (9)) [23]. (TMP)Rh^{II} is a stable metal-centered radical that reacts with CO ($P_{\text{CO}} < 1$ atm) to form a mono CO complex in equilibrium with the CO reductively coupled dimetal diketone complex (Eqs. (10) and (11)) [22]. Formation of the CO reductive coupling product is inhibited by further increases in the porphyrin ligand steric demands such that only the mono-CO complex [(TTiPP)Rh(CO)][•] is detected in the reaction of (TTiPP)Rh^{II} with CO (Eq. (12)) [35]. The metallo-ketone and dimetal diketone complexes contain carbonyl units like those in organic ketones ($\nu_{\text{CO}} \sim 1640\text{--}1760 \text{ cm}^{-1}$) [36]. The mono



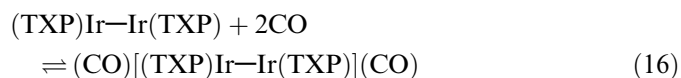
CO-complex [(TMP)Rh(CO)][•] is observed to react with (CH₃)₃Sn–H and styrene (CH₂=CH(C₆H₅)) to produce a formyl complex (TMP)Rh–C(O)–H and (TMP)Rh–C(O)CH₂CH(C₆H₅)C(O)–Rh(TMP) (Eqs. (13) and (14)), respectively, which also contain carbonyl groups similar to organic aldehydes and ketones [22].



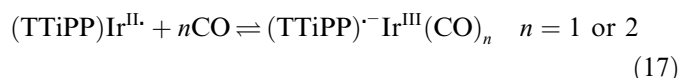
2.4.3. Reactions of (por)Ir^{II} complexes with CO

Iridium(II) porphyrin complexes of OEP and TXP (tetra-xylylporphyrin) occur as Ir^{II}–Ir^{II} bonded dimers and

reactions with CO ($P_{\text{CO}} \sim 1$ atm) form CO adducts as the only observable products (Eqs. (15) and (16)). There is no evidence for metallo-ketone or dimetal diketone complexes. The iridium(II) porphyrin metallo-radical

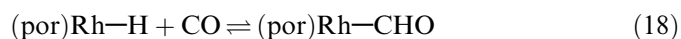


species ((por)Ir^{II}) react with CO ($P_{\text{CO}} \sim 1$ atm) to form complexes where EPR spectra indicate the presence of porphyrin anion radical species (Eq. (17)) [35]

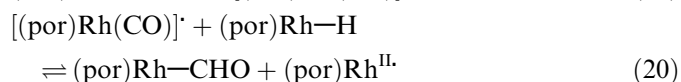
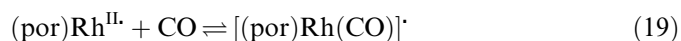


2.4.4. Reactions of (por)M–H with CO (M = Rh, Ir)

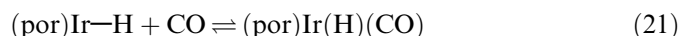
Rhodium porphyrin hydrides react with CO to produce metallo-formyl complexes (Eq. (18)) [37]. The (por)Rh–H reactions are catalyzed by (por)Rh^{II} species and proceed by a radical chain pathway involving



one-electron activated CO (Eqs. (19) and (20)) [37].



Reactions of iridium porphyrin hydrides with CO ($P_{\text{CO}} \sim 1$ atm) produce six coordinate CO adducts ((por)Ir(H)(CO)) as the only observed products (Eq. (21)). There is no evidence for the formation of metallo-formyl complexes of iridium ((por)Ir–CHO or (por)Ir–CHO(CO)) at $P_{\text{CO}} \sim 1$ atm [38].

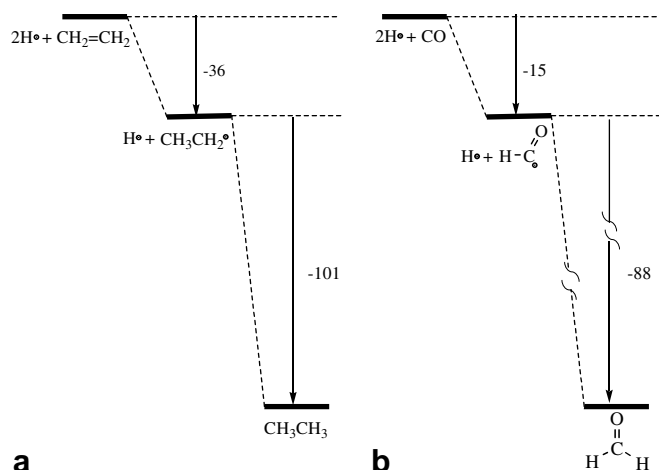


3. Thermodynamic analysis of one-electron activation of ethene and carbon monoxide

3.1. Thermodynamics of one-electron activation of CH₂=CH₂ and CO by hydrogen atom

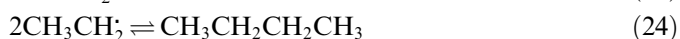
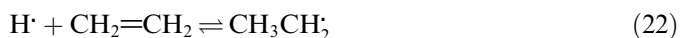
Reactions of hydrogen atoms with ethene and CO illustrate processes where formation of strong H–C bonds result in carbon-centered radicals associated with the complete loss of one π bond for each substrate (CH₃CH₂, H(O)C[•]) (Scheme 1).

Reaction of a hydrogen atom with CH₂=CH₂ to form an ethyl radical (CH₃CH₂[•]) is an example of one-electron activated ethene where the formation of a H–CH₂– bond ($\sim 100 \text{ kcal mol}^{-1}$) justifies the complete loss of the $\sim 64 \text{ kcal mol}^{-1}$ π bond between the two carbon atoms (Scheme 1). The one-electron activated ethyl radical (CH₃CH₂[•]) can subsequently react with another H[•] to form

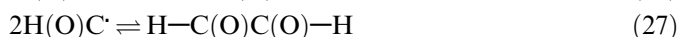


Scheme 1. Enthalpy changes (kcal mol^{-1}) in reaction of H with ethene (a) and carbon monoxide (b) that illustrate formation of carbon centered radicals.

ethane or couple with another ethyl radical to produce butane (Eqs. (22)–(24)). Similarly, hydrogen atoms react with CO to produce the



formyl radical intermediate (Eq. (25)) which subsequently reacts with a second H• to produce formaldehyde (Eq. (26)) or couples to give glyoxal (Eq. (27)). The potential magnitude for the aldehydic C–H bond dissociation enthalpy ($86\text{--}88 \text{ kcal mol}^{-1}$) is large enough to justify the nearly complete rehybridization

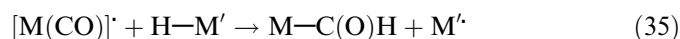
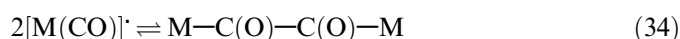
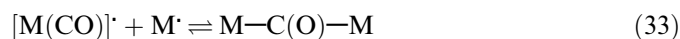
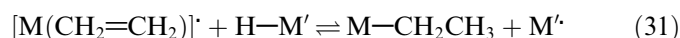
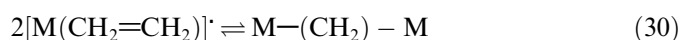
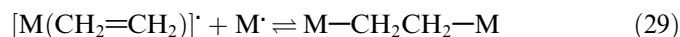
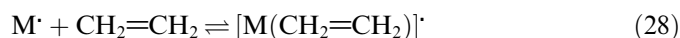


of the CO triple bond to a carbonyl double bond which has a cost of $\sim 70 \text{ kcal mol}^{-1}$. The relatively small exothermicity for ΔH_{25}° ($-15 \text{ kcal mol}^{-1}$) approaches the value for the difference between an aldehydic H–C(O) bond dissociation enthalpy of $\sim 88 \text{ kcal mol}^{-1}$ and the $\sim 70 \text{ kcal mol}^{-1}$ needed to reduce CO triple bond to double bond which is a defining thermodynamic signature for complete one-electron activation of CO.

3.2. Criteria for metallo-radical one-electron activation of ethene and carbon monoxide

Reactions of a single hydrogen atom with $\text{CH}_2=\text{CH}_2$ and $\text{C}\equiv\text{O}$ produce strong H–C bonds ($88\text{--}100 \text{ kcal mol}^{-1}$) which induce carbon-centered radicals ($\text{CH}_3\text{CH}_2^\bullet$, $\text{H}(\text{O})\text{C}^\bullet$) where the substrate π bond order is reduced by one. Reactions of late *d*-transition metal-centered radicals

with ethene and CO to form $[\text{M}(\text{CH}_2=\text{CH}_2)]^\bullet$ and $[\text{M}(\text{CO})]^\bullet$ complexes do not have strong enough M–C bonds to justify the energy change associated with the full loss of a substrate π bond (Eqs. (28) and (32)). For these cases the criteria for $[\text{M}(\text{CO})]^\bullet$ to contain a one-electron activated unit is that the $[\text{M}(\text{CO})]^\bullet$ complex must be able to react in a second one-electron process to produce the near complete loss of a substrate π bond. Several prototype reactions that achieve this criterion of substrate π bond order reduction are illustrated in reactions 29–31, 33–35. Reactions that produce a decrease in the π bond order for $\text{CH}_2=\text{CH}_2$ and $\text{C}\equiv\text{O}$ also result in formal reduction of one or more carbon centers. Reactions



of two M^\bullet with $\text{CH}_2=\text{CH}_2$ and $\text{C}\equiv\text{O}$ that form $\text{M}-\text{CH}_2\text{CH}_2-\text{M}$ and $\text{M}-\text{C}(\text{O})-\text{M}$ bridged complexes have carbon centers that undergo formal reductions from -2 to -3 in $\text{M}-\text{CH}_2\text{CH}_2-\text{M}$ and from $+2$ to 0 in $\text{M}-\text{C}(\text{O})-\text{M}$, respectively. When ethene and CO substrate coupling occurs to form $\text{M}-\text{CH}_2\text{CH}_2-\text{M}$ and $\text{M}-\text{C}(\text{O})-\text{M}$, the reactions are called ethene and carbon monoxide reductive coupling. A thermodynamic feature for sequential M^\bullet reactions with ethene and CO that fulfill this criterion for one-electron activation is that the enthalpy change for the first M^\bullet addition to the substrate will be substantially smaller than that for the second M^\bullet addition.

3.2.1. Thermodynamic criteria for one-electron activation of ethene by rhodium and iridium porphyrin complexes

Guideline thermodynamic criteria for reactions of metal–metal bonded complexes ($\text{M}-\text{M}$) and metalloradicals (M^\bullet) with ethene that produce complexes with reduced bridging $-\text{CH}_2\text{CH}_2-$ units are given in Table 1. It is estimated that the minimum M–C bond dissociation enthalpy for metallo-radicals (M^\bullet) to add with ethene to give $\text{M}-\text{CH}_2\text{CH}_2-\text{M}$ with a fully reduced $-\text{CH}_2\text{CH}_2-$ unit is 40 kcal mol^{-1} (Table 1).

Cobalt(II) porphyrins produce weakly bonded ethene adducts at low temperatures, but no organometallic species like $(\text{por})\text{Co}-\text{CH}_2\text{CH}_2-\text{Co}(\text{por})$ have been detected. The largest measured $(\text{por})\text{Co}$ -organo bond dissociation enthalpies (BDE) are in the range of $33\text{--}36 \text{ kcal mol}^{-1}$ [39–41], which are less than the minimum M–C BDE of $\sim 40 \text{ kcal mol}^{-1}$ required to give a negative ΔG° (298 K) for reaction of metal-centered radicals (M^\bullet) with ethene to form $\text{M}-\text{CH}_2\text{CH}_2-\text{M}$ complexes.

Table 1

Estimated minimum M–C bond dissociation enthalpy required to give a negative ΔG° (298 K) for reactions of M–M and M with $\text{CH}_2=\text{CH}_2$

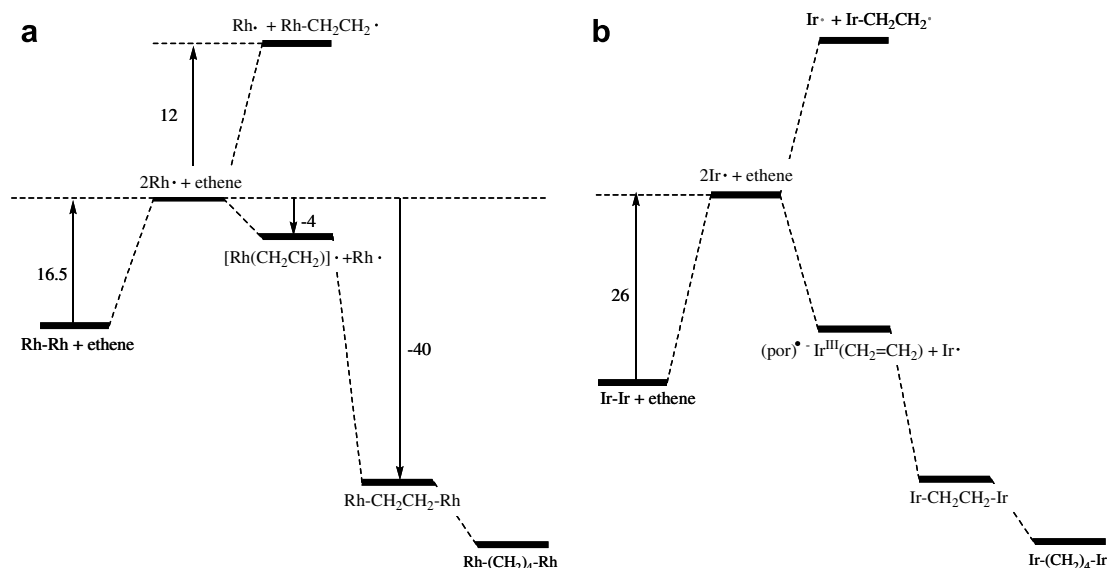
Ethene reaction	ΔG° (298 K) < 0 ^{a,b}
$\text{M}-\text{M} + \text{CH}_2=\text{CH}_2 \rightleftharpoons \text{M}-\text{CH}_2\text{CH}_2-\text{M}$	$2 [\text{M}-\text{CH}_2] > 72 \text{ kcal mol}^{-1} + \text{M}-\text{M}$
$2\text{M}^{\cdot} + \text{CH}_2=\text{CH}_2 \rightleftharpoons \text{M}-\text{CH}_2\text{CH}_2-\text{M}$	$\text{M}-\text{CH}_2 > 40 \text{ kcal mol}^{-1}$
$2\text{M}^{\cdot} + 2\text{CH}_2=\text{CH}_2 \rightleftharpoons \text{M}-(\text{CH}_2)_4-\text{M}$	$\text{M}-\text{CH}_2 > 34 \text{ kcal mol}^{-1}$
$2\text{M}^{\cdot} + 2\text{CO} + \text{CH}_2=\text{CH}_2 \rightleftharpoons \text{M}-\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})-\text{M}$	$\text{M}-\text{C}(\text{O}) > 36 \text{ kcal mol}^{-1}$

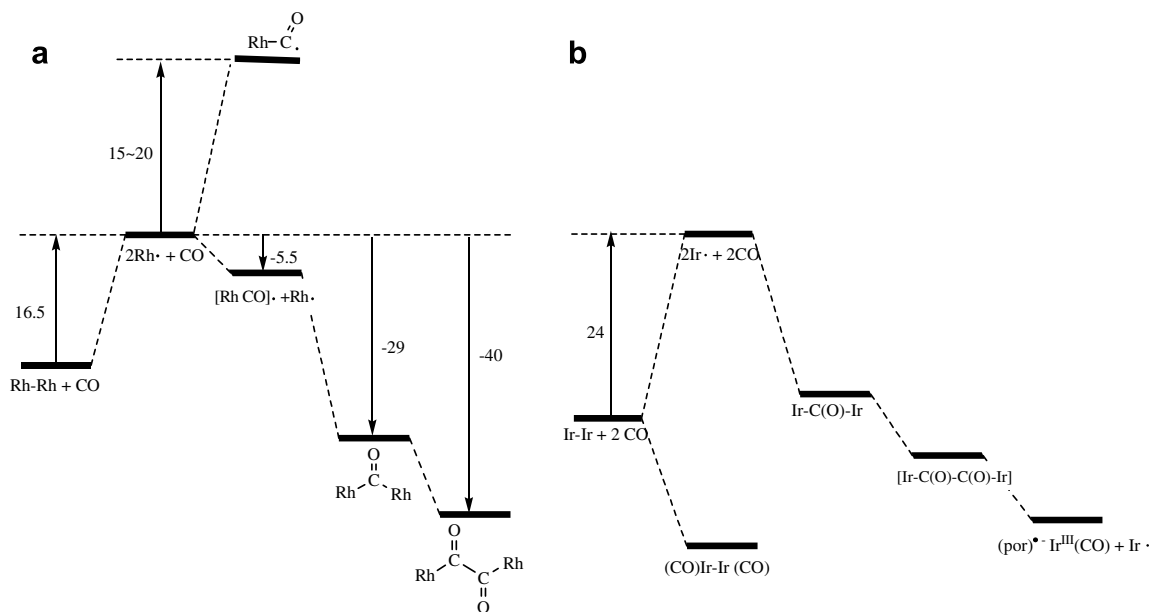
^a $(\text{CH}_2=\text{CH}_2) - (-\text{CH}_2-\text{CH}_2-) \approx 64 \text{ kcal mol}^{-1}$; $(-\text{CH}_2-\text{CH}_2-) = 85 \text{ kcal mol}^{-1}$; $(-\text{O})\text{C}-\text{CH}_2- = 84 \text{ kcal mol}^{-1}$.^b $\Delta S^\circ \approx (27 \times N) \text{ kcal mol}^{-1} \text{ K}^{-1}$ (N = number of products – number of reactants).

(OEP)Rh–Rh(OEP) has a $\text{Rh}^{\text{II}}-\text{Rh}^{\text{II}}$ BDE of $\sim 16 \text{ kcal mol}^{-1}$ and reaction with ethene to form (OEP)Rh– CH_2CH_2 –Rh(OEP) requires a minimum Rh– CH_2 – BDE of $\sim 44 \text{ kcal mol}^{-1}$ (Table 1). Measurements of (por)Rh– CH_3 BDE of 57 kcal mol^{-1} and (por)Rh– CH_2CH_3 BDE of 50 kcal mol^{-1} [7] show that the thermodynamic requirement to produce ethylene bridged derivatives is fulfilled by (por)Rh^{II} complexes (por = OEP, TPP, TXP). The large steric demands of the tetra(2,4,6-triisopropylphenyl) porphyrin derivative (TTiPP) inhibit formation of two- and four-carbon bridged complexes and permit observation of an ethene complex [(TTiPP)Rh^{II}($\text{CH}_2=\text{CH}_2$)]⁺ at low temperatures [24]. The rhodium(II)–ethene complex [(por)Rh^{II}($\text{CH}_2=\text{CH}_2$)]⁺ contains a rhodium(II) site where the unpaired electron is primarily in the rhodium d_{z^2} orbital [24] and definitely is not a localized carbon-centered radical species ((TTiPP)Rh– CH_2CH_2). A (por)Rh CH_2CH_2 carbon centered radical complex is estimated to be about 16 kcal mol^{-1} higher in energy than the observed rhodium(II)–ethene complex (Scheme 2a). Addition of $\text{CH}_2=\text{CH}_2$ with the (por)Rh^{II} to form [(por)Rh^{II}($\text{CH}_2=\text{CH}_2$)]⁺ species has a very small negative ΔH° (-2 to -5 kcal mol^{-1}) (Scheme 2a) [24,35]. Reactions of [(por)Rh^{II}($\text{CH}_2=\text{CH}_2$)]⁺ complexes with a second (por)Rh^{II} unit occur with a much larger ΔH° ($\sim -36 \text{ kcal mol}^{-1}$) compared to the first step ($-4 \pm 2 \text{ kcal mol}^{-1}$) to produce complexes with a fully

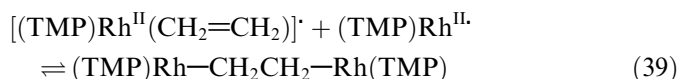
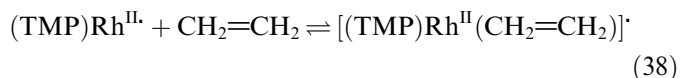
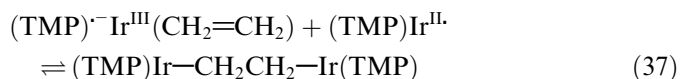
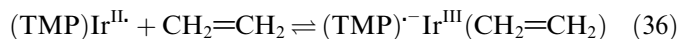
reduced bridging $-\text{CH}_2\text{CH}_2-$ group which fulfills the suggested criteria for having a one-electron activated ethene complex.

(OEP)Ir–Ir(OEP) has an Ir–Ir BDE of $\sim 24 \text{ kcal mol}^{-1}$ and readily reacts with ethene to form (OEP)Ir– CH_2CH_2 –Ir(OEP) and thus the Ir– CH_2 – BDE must be greater than the minimum of 48 kcal mol^{-1} required to give ΔG° (298 K) < 0 (Table 1). (TMP)M^{II} (M = Rh, Ir) also reacts with ethene to form a two-carbon bridged complex ((TMP)M– CH_2CH_2 –M(TMP)), but increasing the porphyrin steric requirement to TTEPP inhibits the two-carbon bridge and ethene coupling is observed to form (TTEPP)M–(CH_2)₄–M(TTEPP) (M = Rh, Ir). The reactions of (TMP)M^{II} (Rh, Ir) and (TTEPP)M^{II} (Rh, Ir) with ethene produce the same type of (CH_2)_{*n*} bridged species but the iridium and rhodium adducts are distinctly different (Eqs. (36) and (38)) (Scheme 3). Reactions of (TMP)Ir^{II} and (TTEPP)Ir^{II} with ethene that pass through an iridium(III) anion radical species illustrate how the anion radicals can reversibly store the radical reactivity (Eqs. (36) and (37)). The (TMP)Rh^{II} and (TTEPP)Rh^{II} ethene reactions proceed through metal-centered radical ethene adducts (Eqs. (38) and (39)) which distinctly contrasts with the iridium porphyrins. Additional increase in the ligand sterics to (TTiPP) inhibits

Scheme 2. Enthalpy changes (ΔH° kcal mol⁻¹) for reactions of (por)M[•] and (por)M–M(por) complexes with ethene: (a) M = Rh(II); (b) M = Ir(II).



Scheme 3. Enthalpy changes (ΔH°) (kcal mol^{-1}) in reaction of (por)M-M(por) and (por)M complexes with carbon monoxide: (a) M = Rh(II); (b) M = Ir(II).



forming the two- and four-carbon bridged complexes and permits observation of ethene adduct formation with the Rh(II) and Ir(II) metal-centered radicals. (TTiPP)Rh^{II} reacts with ethene to form a rhodium(II) ethene adduct with the unpaired electron in d_{z^2} [24], but the (TTiPP)Ir^{III} complex interacts with ethene ($P_{\text{ethene}} \sim 0.5 \text{ atm}$) to form an iridium(III) porphyrin anion radical complex ((TTiPP)^{•-}Ir^{III}(CH₂=CH₂)_n) [25].

3.2.2. Thermodynamic criteria for one-electron activation of CO by rhodium and iridium porphyrin complexes

Guideline thermodynamic criteria for reactions that produce reduction of carbon monoxide to ketone-like units are given in Table 2. The criteria are expressed in terms of the minimum M–C bond dissociation enthalpy that is required for the reaction to have a negative ΔG° (298 K).

(i) *Reactions of (por)Rh^{II} with CO*: Thermodynamic studies for reactions of CO that form [(por)Rh^{II}(CO)], (por)Rh–C(O)–Rh(por), and (por)Rh–C(O)–C(O)–Rh(por) permit constructing an energy diagram for the general reactions of (por)Rh^{II} species with CO (Scheme 3a). A (por)Rh–C(O)– BDE of $\sim 58 \text{ kcal mol}^{-1}$ [42] is a relatively large M–C BDE, but is insufficient to justify loss of

the 70 kcal mol^{-1} π bond ((C≡O)–(C=O) = 70 kcal mol^{-1}) needed to produce a transition metal analog of formyl and acyl radicals which contain carbon centered radicals.

Table 2

Estimated M–C bond dissociation enthalpies to give negative ΔG° (298 K) for reactions of M–M and M with CO

CO reduction	ΔG° (298 K) < 0 ^{a,b}
$\text{M-M} + \text{CO} \rightleftharpoons \text{M}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{M}$	$2\text{M}-\text{C}(\text{O})-\text{O} > 78 \text{ kcal mol}^{-1} + (\text{M}-\text{M})$
$\text{M-M} + 2 \text{CO} \rightleftharpoons \text{M}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{M}$	$2\text{M}-\text{C}(\text{O})-\text{O} > 89 \text{ kcal mol}^{-1} + (\text{M}-\text{M})$
$2 \text{M}^{\cdot} + \text{CO} \rightleftharpoons \text{M}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{M}$	$\text{M}-\text{C}(\text{O})-\text{O} > 43 \text{ kcal mol}^{-1}$
$2 \text{M}^{\cdot} + 2 \text{CO} \rightleftharpoons \text{M}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{M}$	$\text{M}-\text{C}(\text{O})-\text{O} > 48.5 \text{ kcal mol}^{-1}$
$\text{M}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{M} + \text{CO} \rightleftharpoons \text{M}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{M}$	$[\text{M}-\text{C}(\text{O})]^{\cdot-} - [\text{M}-\text{C}(\text{O})] > 5 \text{ kcal mol}^{-1}$
$\text{M-H} + \text{CO} \rightleftharpoons \text{M}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{H}$	$(\text{M}-\text{H}) - (\text{M}-\text{C}(\text{O})\text{H}) < 8 \text{ kcal mol}^{-1}$

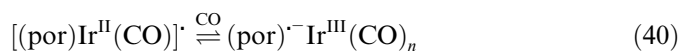
^a (C≡O)–(C=O) = $70 \pm 1 \text{ kcal mol}^{-1}$; C(O)–C(O)– = $67 \pm 3 \text{ kcal mol}^{-1}$.

^b $\Delta S^\circ = (27 \times N) \text{ cal mol}^{-1} \text{ K}^{-1}$ (N = number of products – number of reactants).

The mono carbonyl complex $[(\text{por})\text{Rh}(\text{CO})]^\bullet$ contains a predominantly rhodium-centered unpaired electron (60–70%), and the complex is lower in energy by ~ 20 – 25 kcal mol^{-1} from that of a metallo-formyl radical formulation with a C–O double bond (Scheme 3a). Nevertheless, $[(\text{por})\text{Rh}(\text{CO})]^\bullet$ complexes contain one-electron activated CO because a series of subsequent one-electron reactions produce fully reduced carbonyl units like those in aldehydes and ketones. Rhodium(II) porphyrins are unusual in fulfilling the criteria to produce metallo-ketones $(\text{por})\text{Rh}-\text{C}(\text{O})-\text{Rh}(\text{por})$ and unique in giving favorable thermodynamics to form dimetal diketone complexes $(\text{por})\text{Rh}-\text{C}(\text{O})-\text{C}(\text{O})-\text{Rh}(\text{por})$ through relief of steric strain in the metallo-ketone structure $((\text{por})\text{Rh}-\text{C}(\text{O})-\text{Rh}(\text{por}))$ [23].

(ii) *Reactions of $[(\text{por})\text{Ir}]_2$ and $(\text{por})\text{Ir}^{\text{II}}$ with CO:* The inherent $(\text{por})\text{Ir}-\text{C}(\text{O})-$ bond dissociation enthalpies are expected to be at least as large as those for $(\text{por})\text{Rh}-\text{C}(\text{O})-$ (~ 55 – 59 kcal mol^{-1}), and the absence of observed iridium porphyrin metallo-ketone ($\text{M}-\text{C}(\text{O})-\text{M}$) and dimetal diketone ($\text{M}-\text{C}(\text{O})-\text{C}(\text{O})-\text{M}$) species probably involves factors other than the $\text{M}-\text{C}(\text{O})-$ bond energies. The $\text{Ir}^{\text{II}}-\text{Ir}^{\text{II}}$ bonding and CO adduct energetics apparently make $(\text{CO})[(\text{OEP})\text{Ir}-\text{Ir}(\text{OEP})](\text{CO})$ and $(\text{CO})[(\text{TXP})\text{Ir}-\text{Ir}(\text{TXP})](\text{CO})$ ($P_{\text{CO}} \sim 1 \text{ atm}$) thermodynamically favorable relative to the CO insertion products and intra-molecular oxidation of iridium(II). The ultimate thermodynamic limitation on reactions of iridium(II) porphyrins with CO most probably is the thermodynamic stability of $(\text{por})^-\text{Ir}^{\text{III}}(\text{CO})_n$ species that result from electron transfer from the iridium(II) center to the porphyrin LUMO (π^*) and strong bonding of CO to the iridium(III) center. The CO insertion products $(\text{por})\text{Ir}-\text{C}(\text{O})-\text{Ir}(\text{por})$ and $(\text{por})\text{Ir}-\text{C}(\text{O})-\text{C}(\text{O})-\text{Ir}(\text{por})$ in the presence of CO ($P_{\text{CO}} \sim 1 \text{ atm}$) must be thermodynamically unfavorable relative to $(\text{por})^-\text{Ir}^{\text{III}}(\text{CO})_2$ species (Scheme 3b). The lower energy position of the porphyrin LUMO (π^*) relative to the d_{z^2} in iridium(II) adducts makes porphyrin ligands redox non-innocent in iridium(II)–CO reactions. In order for iridium(II) complexes to form metallo-ketone and dimetal diketone complexes, ligands with higher energy π^* orbitals are needed. The recently reported iridium complex of *N,N,N*-tri(6-methyl-2-pyridylmethyl)amine $[(\text{Me}_3\text{tpa})\text{Ir}]^{2+}$ [2] is a possible candidate to achieve reactions with CO that form complexes with reduced CO units.

(iii) *Reactions of $(\text{por})\text{M}-\text{H}$ and CO to form $(\text{por})\text{M}-\text{CHO}$ or $(\text{por})\text{M}(\text{H})(\text{CO})$:* Absence of observed reactions of $(\text{por})\text{Ir}-\text{H}$ species with CO to produce formyl complexes $((\text{por})\text{Ir}-\text{CHO}$, $(\text{por})\text{Ir}-\text{CHO}(\text{CO}))$ could be either of kinetic or thermodynamic origin. The iridium porphyrin species that has a composition like that of $[(\text{por})\text{Rh}(\text{CO})]^\bullet$ contains a reduced porphyrin unit and iridium(III) $((\text{por})^-\text{Ir}^{\text{III}}(\text{CO}))$ (Eq. (40)) which could shut down the radical chain pathway observed in the formation of $(\text{por})\text{Rh}-\text{CHO}$ complexes [37]. There are now many examples of $(\text{por})\text{Rh}-\text{H}$ complexes



that react with CO ($P_{\text{CO}} \sim 1 \text{ atm}$, $T = 298 \text{ K}$) to produce metallo-formyl complexes $((\text{por})\text{Rh}-\text{CHO})$ as the thermodynamic products. One of the thermodynamic criteria for reaction of a metal hydride ($\text{M}-\text{H}$) with CO to produce a metallo-formyl ($\text{M}-\text{CHO}$) ($\Delta G^\circ (298 \text{ K}) < 0$) is that the $\text{M}-\text{H}$ BDE should be no more than $\sim 8 \text{ kcal mol}^{-1}$ larger than the $\text{M}-\text{CHO}$ BDE (Table 2). Thermodynamic studies place the $(\text{por})\text{Rh}-\text{H}$ at $61 \pm 1 \text{ kcal mol}^{-1}$ [7] and $(\text{por})\text{Rh}-\text{CHO}$ at $\sim 58 \pm 2 \text{ kcal mol}^{-1}$ [42] so that the $(\text{por})\text{Rh}$ system comfortably fulfills this thermodynamic criterion. The absence of observed $(\text{por})\text{Ir}-\text{CHO}$ species in reactions of $(\text{por})\text{Ir}-\text{H}$ with CO probably results from the $(\text{por})\text{Ir}-\text{H}$ BDE being more than 8 kcal mol^{-1} larger than the $(\text{por})\text{Ir}-\text{CHO}$ BDE. A more complete understanding of the iridium porphyrin substrate reactions must await results of thermodynamic studies that are in progress.

4. Summary

Reactions of cobalt(II) porphyrins with ethene and CO form weakly bonded 1:1 adducts that have not yet been observed to react further to form any complexes containing reduced substrate units. The inability of cobalt(II) porphyrins to produce complexes with reduced ethene and CO fragments like $-\text{CH}_2\text{CH}_2-$ and $-\text{C}(\text{O})-$ is easily understood in terms of the Co–C bond dissociation enthalpies ($\text{Co}-\text{C} < 36 \text{ kcal mol}^{-1}$) which are too small to fulfill the thermodynamic criteria for producing these types of reactions ($\text{M}-\text{C} > 40 \text{ kcal mol}^{-1}$).

Rhodium(II) porphyrin metal-centered radicals form 1:1 weakly bonded complexes with ethene and CO that function as productive intermediates in reactions that reduce and couple ethene and CO. The $(\text{por})\text{Rh}-\text{CH}_2-$ ($\sim 50 \text{ kcal mol}^{-1}$) and $(\text{por})\text{Rh}-\text{C}(\text{O})-$ ($\sim 58 \text{ kcal mol}^{-1}$) bond dissociation enthalpies are too small for one $(\text{por})\text{Rh}^{\text{II}}$ -substrate bond to justify the full rehybridization of ethene and CO to localized carbon centered radicals ($\text{M}-\text{CH}_2\text{CH}_2$; $\text{M}-(\text{O})\text{C}^\bullet$). Formation of two $\text{Rh}^{\text{II}}-\text{C}$ bonds is needed to attain favorable thermodynamics for reduction of ethene and CO to species like $\text{Rh}-\text{CH}_2\text{CH}_2-\text{Rh}$, $\text{Rh}-(\text{CH}_2)_4-\text{Rh}$, $\text{Rh}-\text{C}(\text{O})-\text{Rh}$, and $\text{Rh}-\text{C}(\text{O})-\text{C}(\text{O})-\text{Rh}$. The 1:1 complexes $[(\text{por})\text{Rh}(\text{CH}_2\text{CH}_2)]^\bullet$, $[(\text{por})\text{Rh}(\text{CO})]^\bullet$ formed by reactions of $(\text{por})\text{Rh}^{\text{II}}$ with ethene and CO are primarily rhodium(II) metal-centered radicals that are poised for a second one-electron reaction that completes the substrate reduction and binding. The 1:1 complexes of $(\text{por})\text{Rh}^{\text{II}}$ with ethene and CO are not properly described as localized substrate carbon-centered radicals, but they do contain one-electron activated substrates because a second one-electron reaction results in substrate reduction. Ethene and CO reduction is accomplished by reaction with one hydrogen atom because of the strong C–H bonding, but reactions of two rhodium(II) metallo-centered radicals are needed to accomplish full substrate reductions.

Iridium(II) porphyrin complexes reduce ethene in forming (por)Ir–CH₂CH₂–Ir(por) and (por)Ir–(CH₂)₄–Ir(por), but no iridium porphyrin complexes containing reduced CO units like those in metallo-ketones (M–C(O)–M) have been observed. The (por)Ir–C(O)– bond dissociation enthalpies are undoubtedly at least as large as the (por)Rh–C(O)– BDE, but reactions of (por)Ir^{II} with CO do not result in complexes with reduced CO units. The combination of Ir^{II}–Ir^{II} bonding and CO adduct formation for lower steric demand porphyrins places (CO)[(por)Ir–Ir(por)](CO) at lower energy than species like the metallo-ketone M–C(O)–M (Scheme 3b). Ethene and CO 1:1 complex formation with monomeric (por)Ir^{II} metallo-radical species results in intra-molecular electron transfer to form iridium(III) porphyrin anion radical species ((por)^{•–}Ir^{III}(CH₂=CH₂)_n, (por)^{•–}Ir^{III}(CO)_n). Formation of the porphyrin anion radical complex is not necessarily irreversible as illustrated by reaction of (por)^{•–}Ir^{III}(CH₂=CH₂) with a second (por)Ir^{II} to form (por)Ir–CH₂CH₂–Ir(por). In the case of CO substrate the (por)^{•–}Ir^{III}(CO)_n complex does not react with a second (por)Ir^{II} to form (por)Ir–C(O)–Ir(por). Either the (por)^{•–}Ir^{III}(CO)_n complex is kinetically trapped or it is thermodynamically favored over CO reduced species like (por)Ir–C(O)–Ir(por) and (por)Ir–C(O)–C(O)–Ir(por). The relative ease of (por)Ir^{II} oxidation and the redox non-innocence of the porphyrin macrocycle through the energy position of the porphyrin π* has a major influence on the scope of (por)Ir^{II} reactions with CO. Observation of iridium metallo-ketone (L)Ir–C(O)–Ir(L) and dimetal diketone (L)Ir–C(O)–C(O)–Ir(L) species require using a ligand (L) which does not give intra-molecular oxidation of iridium(II). The recently reported iridium complexes of [(Me₃tpa)Ir]²⁺ [2] are promising candidates to manifest this type of reactivity.

Acknowledgements

This research was supported by the Department of Energy, Division of Chemical Sciences and Office of Science through Grant DE-FG02-86ER-13615.

References

- [1] D. Astruc, *Electron-Transfer and Radical Processes in Transition Metal Chemistry*, VCH, Weinheim, Germany, 1995.
- [2] D.G.H. Hetterscheid, J. Kaiser, E. Reijerse, T.P.J. Peters, S. Thewissen, A.N.J. Blok, J.M.M. Smits, R. De Gelder, B. De Bruin, *J. Am. Chem. Soc.* 127 (2005) 1895–1905.
- [3] R. Poli, *Chem. Rev.* 96 (1996) 2135–2204.
- [4] L.A. MacAdams, G.P. Buffone, C.D. Incarvito, J.A. Golen, A.L. Rheingold, K.H. Theopold, *Chem. Commun.* (2003) 1164–1165.
- [5] C. Pariya, K.H. Theopold, *Curr. Sci.* 78 (2000) 1345–1351.
- [6] K.E. Torraca, L. McElwee-White, *Coord. Chem. Rev.* 206–207 (2000) 469–491.
- [7] W.H. Cui, B.B. Wayland, *J. Am. Chem. Soc.* 126 (2004) 8266–8274.
- [8] W.H. Cui, X.P. Zhang, B.B. Wayland, *J. Am. Chem. Soc.* 125 (2003) 4994–4995.
- [9] D.G.H. Hetterscheid, M. Bens, B. de Bruin, *J. Chem. Soc., Dalton Trans.* (2005) 979–984.
- [10] R. Poli, M. Baya, R. Meunier-Prest, S. Raveau, *New J. Chem.* 30 (2006) 759–773.
- [11] S.K. Yeung, K.S. Chan, *Organometallics* 24 (2005) 6426–6430.
- [12] K.W. Mak, S.K. Yeung, K.S. Chan, *Organometallics* 21 (2002) 2362–2364.
- [13] B. de Bruin, P.H.M. Budzelaar, A.W. Gal, *Angew. Chem., Int. Ed. Engl.* 43 (2004) 4142–4157.
- [14] J.R. Krumper, M. Gerisch, J.M. Suh, R.G. Bergman, T.D. Tilley, *J. Org. Chem.* 68 (2003) 9705–9710.
- [15] D.G.H. Hetterscheid, B. de Bruin, *J. Mol. Catal. A: Chem.* 251 (2006) 291–296.
- [16] B.B. Wayland, C.-H. Peng, X. Fu, Z. Lu, M. Fryd, *Macromolecules* 39 (2006) 8219–8222.
- [17] Z. Lu, M. Fryd, B.B. Wayland, *Macromolecules* 37 (2004) 2686–2687.
- [18] R. Poli, *Angew. Chem., Int. Ed. Engl.* 45 (2006) 5058–5070.
- [19] B. de Bruin, D.G.H. Hetterscheid, *Eur. J. Inorg. Chem.* (2007) 211–230.
- [20] B. Wayland, X. Fu, *Science* 311 (2006) 790–791.
- [21] O.T. Summerscales, F.G.N. Cloke, P.B. Hitchcock, J.C. Green, N. Hazari, *Science* 311 (2006) 829–831.
- [22] B.B. Wayland, A.E. Sherry, G. Poszmik, A.G. Bunn, *J. Am. Chem. Soc.* 114 (1992) 1673–1681.
- [23] V.L. Coffin, W. Brennen, B.B. Wayland, *J. Am. Chem. Soc.* 110 (1988) 6063–6069.
- [24] A.G. Bunn, B.B. Wayland, *J. Am. Chem. Soc.* 114 (1992) 6917–6919.
- [25] H.L. Zhai, A. Bunn, B. Wayland, *Chem. Commun.* (2001) 1294–1295.
- [26] B.B. Wayland, J.V. Minkiewicz, M.E. Abd-Elmagged, *J. Am. Chem. Soc.* 96 (1974) 2795–2801.
- [27] G.N. La Mar, F.A. Walker, *J. Am. Chem. Soc.* 95 (1973) 1790–1796.
- [28] H. Ogoshi, J. Setsune, Z. Yoshida, *J. Am. Chem. Soc.* 99 (1977) 3869–3870.
- [29] K.J. Del Rossi, X.X. Zhang, B.B. Wayland, *J. Organomet. Chem.* 504 (1995) 47–56.
- [30] B.B. Wayland, V.L. Coffin, M.D. Farnos, *Inorg. Chem.* 27 (1988) 2745–2747.
- [31] D.C. Woska, B.B. Wayland, *Inorg. Chim. Acta* 270 (1998) 197–201.
- [32] M.-S. Liao, S. Scheiner, *J. Chem. Phys.* 114 (2001) 9780–9791.
- [33] B.B. Wayland, A.E. Sherry, A.G. Bunn, *J. Am. Chem. Soc.* 115 (1993) 7675–7684.
- [34] A.G. Bunn, Ph.D. Thesis, University of Pennsylvania, Philadelphia, 1993.
- [35] L. Basicckes, A.G. Bunn, B.B. Wayland, *Can. J. Chem.* 79 (2001) 854–856.
- [36] R.M. Silverstein, F.X. Webster, D.J. Kiemle, *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, Hoboken, NJ, 2005.
- [37] R.S. Paonessa, N.C. Thomas, J. Halpern, *J. Am. Chem. Soc.* 107 (1985) 4333–4335.
- [38] M.D. Farnos, B.A. Woods, B.B. Wayland, *J. Am. Chem. Soc.* 108 (1986) 3659–3663.
- [39] M.K. Geno, J. Halpern, *J. Am. Chem. Soc.* 109 (1987) 1238–1240.
- [40] D.C. Woska, Z.L.D. Xie, A.A. Gridnev, S.D. Ittel, M. Fryd, B.B. Wayland, *J. Am. Chem. Soc.* 118 (1996) 9102–9109.
- [41] A. Qiu, D.T. Sawyer, *J. Porphyrins Phthalocyanines* 1 (1997) 125–134.
- [42] B.B. Wayland, *NATO ASI Ser. C* 367 (1992) 69–74.