Equilibrium thermodynamic studies for the formation of 1:1 complexes of CO and ethene with a rhodium(II) porphyrin metallo-radical

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Abstract: Tetra(2,4,6 triisopropropyl phenyl)porphyrinatorhodium(II) ((TTiPP)Rh^{II}·1) is a persistent metal-centered radical with the odd electron in the rhodium(II) dz^2 orbital. (TTiPP)Rh^{II}· forms 1:1 complexes with CO and CH₂CH₂ where the porphyrin ligand steric properties inhibit further reactions of the one-electron activated substrates. ¹H NMR paramagnetic shifts at a series of temperatures are used in evaluating the thermodynamics for CO complex formation with 1 to form [(TTiPP)Rh^{II}(CO)]·2 ($\Delta H^\circ = -5.5 \pm 0.5 \text{ kcal mol}^{-1}$; $\Delta S^\circ = -9 \pm 1 \text{ cal K}^{-1} \text{ mol}^{-1}$). Related ¹H NMR studies show that the bonding of 1 with ethene is less favorable than CO.

Key words: rhodium porphyrin, carbon monoxide, ethene, thermodynamics, complex formation, metal-centered radical.

Résumé : Le tétra(2,4,6-triisopropylphényl)porphyrinatorhodium(II) ((TTiPP)Rh^{II}·1) est un radical persistant centré sur un métal comportant un électron célibataire dans l'orbitale dz^2 du rhodium(II). Le (TTiPP)Rh^{II}· forme des complexes 1:1, avec le CO et le CH₂CH₂, dans lesquels les propriétés stériques du ligand porphyrine empêchent d'autres réactions avec des substrats à un électron activés. On a utilisé les déplacements paramagnétiques en RMN du ¹H à une série de températures pour évaluer les facteurs thermodynamiques de la réaction entre CO et 1 pour conduire à la formation du complexe [(TTiPP)Rh^{II}(CO)]·2 ($\Delta H^\circ = -5,5 \pm 0,5$ kcal mol⁻¹; $\Delta S^\circ = -9 \pm 1$ cal K⁻¹ mol⁻¹). D'autres études de RMN du ¹H montrent que la liaison entre 1 et l'éthène est moins favorable que celle avec le CO.

Mots clés : porphyrine-rhodium, monoxyde de carbone, éthène, thermodynamique, formation de complexe, radical centré sur un métal.

[Traduit par la Rédaction]

Introduction

Carbon monoxide and ethene are most often activated by binding with Lewis acid metal centers that promote twoelectron reactions of nucleophiles at a substrate carbon site. The binding of carbon monoxide and ethene with rhodium(II) porphyrin metal-centered radicals results in complexes that manifest an alternate pattern of reactivity associated with one-electron activated substrates (1-6). Reactions of CO and ethene with rhodium(II) porphyrins that yield substrate bridged (Rh-C(O)-Rh (3, 4), Rh-CH₂CH₂-Rh (7, 8)) and coupled species (Rh-C(O)-C(O)-Rh (1-3), Rh-CH₂CH₂-CH₂CH₂-Rh (5, 6)) illustrate one-electron activated carbon centers in CO and ethene ligands. Direct investigation of complexes with one-electron activated substrates is usually precluded because they are highly reactive transient intermediates. However, steric constraints can be built into the porphyrin ligand which inhibit access to the reactive sub-

Received September 15, 2000. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on June 30, 2001.

This paper is dedicated to Professor Brian James on the occasion of his 65^{th} birthday.

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strate site and provide persistent complexes containing oneelectron activated CO and ethene (2, 5).

Tetra(2,4,6 triisopropyl phenyl)porphyrinatorhodium(II) ((TTiPP)Rh^{II}.) is an example of a metal-centered radical where the structural features sterically preclude Rh^{II}—Rh^{II} bonding and inhibit CO and ethene substrate reactions. This article reports on measurements of equilibrium thermodynamic values for complex formation of (TTiPP)Rh^{II}. with carbon monoxide and ethene.

Results and discussion

(TTiPP)Rh^{II} **1** is a stable persistent metal-centered radical with a $(d_{xy})^2 (d_{xz,yz})^4 (d_{z2})^1$ electron configuration as shown by the EPR spectral parameters in toluene glass (90 K) ($g_{xx} = g_{yy} = 2.82, g_{zz} = 1.85$) (9). ¹H NMR chemical shifts for (TTiPP)Rh^{II} in toluene- d_8 solutions manifest an inverse dependence on temperature (T = 190-330 K) that is characteristic of Curie–Weiss paramagnetism (Fig. 1). There is no evidence from ¹H NMR, electronic spectra, or EPR for dimerization of (TTiPP)Rh^{II} through Rh^{II}—Rh^{II} bonding in toluene solution (190–330 K) or frozen glass (160–90 K). The steric constraints for the TTiPP porphyrin ligand preclude dimerization through Rh^{II}—Rh^{II} bonding which occurs with less sterically demanding porphyrin ligands such as tetraphenyl porphyrin ([(TPP)Rh]₂) (10).

The EPR spectrum in toluene glass (90 K) for (TTiPP)Rh^{II}· in contact with ¹³CO demonstrates the formation of a mono CO complex ([(TTiPP)Rh^{II}(CO)]·) through splitting of each

Fig. 1. Temperature dependence for the pyrrole ¹H NMR paramagnetic shift (δ (ppm)) for toluene- d_8 solutions of (TTiPP)Rh^{II}. (\blacksquare), (TTiPP)Rh^{II}. (\bullet) in contact with CH₂CH₂ (0.25 atm (1 atm = 101.325 kPa)), and (TTiPP)Rh^{II}. (\blacktriangle) in contact with CO (0.855 atm (1 atm = 101.325 kPa)).



of the three g value transitions into a doublet by ${}^{13}C$ (9). The observed pyrrole ¹H NMR paramagnetic shifts for toluene- d_8 solutions of $(TTiPP)Rh^{II} \cdot 1 (1.0 \times 10^{-3} \text{ M})$ in contact with carbon monoxide ($P_{CO} = 0.855$ atm (1 atm = 101.325 kPa)) are plotted vs. the inverse of temperature (T = 180-300 K)in Fig. 1. Sections of linearity are observed in both the higher and lower temperature regimes. The observed pyrrole chemical shifts in the higher temperature linear region coincide with the values for (TTiPP)Rh^{II} ($\delta_1 = -1.86 + 3334 \text{ T}^{-1}$) and the lower temperature linear portion is assigned to the limiting shift values for a mono carbonyl complex $([(TTiPP)Rh^{II}(CO)] \cdot 2 \ (\delta_2 = -2.72 + 2376T^{-1})).$ The ratio of the slope of the pyrrole hydrogen paramagnetic shifts vs. T^{-1} plots for [(TTiPP)Rh^{II}(CO)]· to that for (TTiPP)Rh^{II}· equals 0.71 and this value is proportional to the ratio of the electron-pyrrole hydrogen coupling constants $A_{\rm H}$ (2)/ $A_{\rm H}$ (1) and related pyrrole hydrogen spin densities (11). This ratio of the porphyrin pyrrole electron-hydrogen coupling constants (0.71) is similar to the ratio of 0.65 for the total rhodium spin density of $[(TTiPP)Rh^{II}(CO)]$ (0.62) to that of the $(TTiPP)Rh^{II}$. (0.95) which were estimated from EPR studies (9). In the temperature regime between 270 and 330 K, substantial amounts of both (TTiPP)Rh^{II}· and [(TTiPP)Rh^{II}(CO)]· are present in equilibrium with CO (eq. [1]). The

$$[1] \qquad [(TTiPP)Rh^{II}] \cdot + CO \rightleftharpoons [(TTiPP)Rh^{II}(CO)] \cdot$$

Fig. 2. van't Hoff plot for reaction of $(TTiPP)Rh^{II}$. with CO in toluene- $d_{8^{\circ}}$.



observed pyrrole shifts in this temperature range correspond to the mol fraction averaged positions for the (TTiPP)Rh^{II}. and [(TTiPP)Rh^{II}(CO)]. species in limiting fast exchange.

The pyrrole chemical shifts determined for (TTiPP)Rh^{II}·1 $(\delta_1 = -1.86 + 3334 \text{ T}^{-1})$ and $[(\text{TTiPP})\text{Rh}^{\text{II}}(\text{CO})] \cdot 2 (\delta_2 = -2.72 + 1000 \text{ C})$ 2376 T⁻¹) were used in determining the fraction of monocarbonyl complex from the observed mol fraction averaged chemical shifts $(\delta_{obs} = N(1)\delta(1) + N(2)\delta(2)), N(2) = [2]/[1] + (1-1)\delta(2)$ [2]). The equilibrium constant expression for rxn. [1] ($K_1 =$ [[(TTiPP)Rh^{II}(CO)]·]/[(TTiPP)Rh^{II}·][CO]) is evaluated using the ratio of mol fractions N(2):N(1) and the molar concentration of CO at each temperature (T). The plot of $\ln K_1$ vs. T⁻¹ (Fig. 2) gives an enthalpy change (ΔH_1°) of -5.5 ± 0.5 kcal mol⁻¹ and entropy change (ΔS_1°) of -9 ± 1 cal K⁻¹ mol⁻¹ for the reaction of (TTiPP)Rh^{II}. with CO to form [(TTiPP)Rh^{II}(CO)]· (eq. [1]). The enthalpy change for complex formation of 1 with CO ($\Delta H_1^{\circ} = -5.5 \pm 0.5$ kcal mol⁻¹) is very small even when compared to the reaction of CO with a related Rh^{II}—Rh^{II} bonded dimer [(OEP)Rh]₂ to form the mono CO adduct [(OEP)Rh]₂CO ($\Delta H^{\circ} = -12 \text{ kcal mol}^{-1}$) (3).

Reaction of $(TTiPP)Rh^{II}$ with ethene produces a 1:1 complex $[(TTiPP)Rh^{II}(CH_2CH_2)]$ ·3 that is kinetically *meta*-stable relative to an ethene coupling product $(Rh-(CH_2)_4-Rh)$.

$$[2] \quad [(TTiPP)Rh^{II}] \cdot + CH_2CH_2 \\ \rightleftharpoons [(TTiPP)Rh^{II}(CH_2CH_2)] \cdot$$

The g_{zz} transition in the EPR spectrum for the ${}^{13}C_2H_4$ derivative of **3** (90 K) occurs as a triplet of doublets arising from coupling of two equivalent ${}^{13}C$ nuclei on each ${}^{103}Rh$ transition which demonstrates that **3** is a 1:1 complex, [(TTiPP)Rh^{II}(CH₂CH₂)]· (5).

¹H NMR chemical shifts for the pyrrole hydrogens of (TTiPP)Rh^{II}. in contact with ethene (0.25 atm (1 atm = 101.325 kPa)) in toluene- d_8 over a wide range of tempera-

tures is shown in Fig. 1. At temperatures above 220 K the observed pyrrole ¹H NMR shifts are indistinguishable from the values for (TTiPP)Rh^{II.} and only below 200 K is there a clear indication of ethene complex formation with **1** to form **3**. Only a small temperature range is available for the study of **3** forming in toluene solutions and the regime with the limiting shift values and thus complete conversion to **3** was not attained. Qualitatively, the thermodynamics of ethene coordination with **1** are substantially less favorable than CO complexation.

Experimental

The synthesis of (TTiPP) has been described previously (2). All manipulations were performed under argon or by vacuum techniques. Reagents were purchased from Aldrich or Strem. Research grade carbon monoxide and ethene (Matheson) and ¹³C-labeled carbon monoxide and ethene (Aldrich) were used without further purification. Benzene and toluene solvents used in the EPR and NMR studies were degassed, refluxed over sodium benzophenone, and then degassed again by freeze–pump–thaw cycles.

NMR Studies

Proton NMR spectra were recorded using a Bruker AF500 instrument equipped with a variable temperature FTS Refrigerator unit. NMR samples used toluene- d_8 as the solvent in a sealed NMR tube and low temperatures were obtained by utilizing the boil-off from liquid nitrogen. Temperature calibration was obtained by using methanol or ethylene glycol as an external standard.

Reaction of (TTiPP)Rh^{II}. with CO-CH₂CH₂

In a typical experiment, $(TTiPP)Rh^{II}$. was generated by photolysis of a benzene solution of $(TTiPP)Rh-CH_3$ (1 × 10⁻³ M) in a vacuum adapted NMR tube. Samples of $(TTiPP)Rh^{II}$. in vacuum adapted NMR tubes were then pressurized with CO (0.86 atm (1 atm = 101.325 kPa)) or ethene (0.25 atm (1 atm = 101.325 kPa)) and sealed. The solubility of CO and ethene in toluene was determined as a function of temperature. When measuring the concentration of disolved gas in solution at a temperature T_2 , P is the pressure in atm (1 atm = 101.325 kPa) at the laboratory temperature T_1 in K when the gas was added into the tube. ([CO] (12) = $[a + b(T_2)][P][T_1/T_2]$ (*a* and *b* are solvent dependent in toluene, $a = 4.405 \times 10^{-3}$ and $b = 1.085 \times 10^{-5}$); ([CO] (303 K) in toluene = 6.5×10^{-3} M), [ethene] (13) = $-0.4906 + (0.1850T_2)P$. ([ethene] (303 K) in toluene = 3.0×10^{-2} M).

Acknowledgements

This research was supported by grants from the Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, Grant DE-FG02–86ER 13615, and the National Science Foundation.

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