

Numerical Treatment of In-Situ Data for the Pre-Catalytic Transformations of Rhodium Carbonyl Species and Implications.

Ayman D. Allian and Chew Wee*

Department of Chemical and Biomolecular Engineering
4 Engineering Drive 4
National University of Singapore
SINGAPORE 117576

Keywords: Rhodium Carbonyl clusters, Carbonyl scrambling, in situ FTIR, chemometrics

Prepared for Poster at the 2004 Annual Meeting AIChE

Copyright © Ayman D. Allian and Chew Wee*
National University of Singapore

November 2004

Unpublished

AIChE Shall Not Be Responsible For Statements or Opinions Contained in Papers or Printed in its Publications

Abstract

Abstract: In-situ FTIR spectroscopy at 1 cm^{-1} resolution was conducted on n-hexane solutions of $\text{Rh}_4(\sigma\text{-CO})_9(\mu\text{-CO})_3$ on the interval $T=268\text{-}288\text{ K}$ and $PT=0.1\text{-}7.0\text{ MPa}$ using either helium or carbon monoxide as dissolved gas. Analysis of the spectral data sets was conducted using BTEM in order to recover the pure component spectra. A new spectral pattern was recovered with terminal vibrations at 2041, 2043, 2069.8 and 2075 cm^{-1} . The new spectrum indicates the presence of either one all terminal structure $\text{Rh}_4(\sigma\text{-CO})_{12}$ with quasi T symmetry, or the co-existence of two highly symmetrical terminal geometries with similar free energies. The equilibrium between $\text{Rh}_4(\sigma\text{-CO})_{12}$ and $\text{Rh}_4(\sigma\text{-CO})_9(\mu\text{-CO})_3$ was determined in the presence of both helium and CO. The equilibrium constant $K = [\text{Rh}_4(\sigma\text{-CO})_{12}]/[\text{Rh}_4(\sigma\text{-CO})_9(\mu\text{-CO})_3]$ at standard conditions was circa 0.011 and the determined equilibrium parameters were $\Delta_rG = 12.63 \pm 4.8\text{ kJ / mole}$, $\Delta_rH = -21.45 \pm 2.3\text{ kJ/mole}$ and $\Delta_rS = -114.3 \pm 8.35\text{ J/mole K}$. As anticipated, the free energy difference is very low, and the unbridged isomers have a lower entropy – consistent with a higher symmetry. This finding helps to address a long-standing issue concerning the existence of various $\text{M}_4(\sigma\text{-CO})_{12}$ symmetries. Pure component spectra of other known rhodium complexes, namely, $\text{Rh}_2(\sigma\text{-CO})_6(\mu\text{-CO})_2$ and $\text{Rh}_6(\sigma\text{-CO})_{12}(\mu^3\text{-CO})_4$ were also recovered. No conclusive evidence for the postulated species $\text{Rh}_2(\sigma\text{-CO})_8$ nor $\text{Rh}_4(\sigma\text{-CO})_8(\mu\text{-CO})_4$ could be obtained.

1.0 Introduction

The group VIII (Co, Rh, Ir) tetranuclear metal carbonyl clusters $M_4(CO)_{12}$ have been the subject of intense research for over 40 years. In particular, their structures and fluxional behavior in solution has generated considerable discussion^{1,2,3,4,5,6}.

The rhodium cluster $Rh_4(\sigma-CO)_9(\mu-CO)_3$ represents a special case due in part to its highly fluxional behavior. The x-ray structure has been determined on at least 3 occasions, and an idealized C_{3v} symmetric icosahedral has been shown^{7,8}. In solution, the infrared spectra are consistent with the same geometry at room temperature³. In addition, the ^{13}C NMR³ and ^{103}Rh solution spectra⁹ are also consistent with the bridged C_{3v} symmetric icosahedral geometry at least in the vicinity of 213 K. However, at circa 268 K coalescence occurs^{1,3} indicating equivalence of all CO on the NMR time scale. This suggests the inter-conversion: $C_{3v} \leftrightarrow$ all-terminal $\leftrightarrow C_{3v}$ ^{1,3,4,5}. However, to date the presence of the all terminal species have not been confirmed.

In the present contribution the solution chemistry of $Rh_4(CO)_{12}$ is re-investigated under various helium or CO partial pressures in n-hexane as solvent on the interval $T=268-288$ K and $P_T=0.1-7.0$ MPa using FTIR as the spectroscopic tool and BTEM as the signal processing algorithm^{10,11}. BTEM has repeatedly shown its ability to retrieve pure component spectra from very weak signal intensities, i.e. for $HRh(CO)_4$ ¹².

2.0 Results and Discussion

BTEM successfully resolved the pure component spectra of $Rh_6(CO)_{16}$, $Ni(CO)_4$ and $Fe(CO)_5$ (impurities from gas cylinders), and their time dependent concentration were obtained. In addition and for the first time the fragmentation of the $Rh_4(\sigma-CO)_9(\mu-CO)_3$ to $Rh_2(\sigma-CO)_6(\mu-CO)_2$ was unequivocally observed at mild temperatures and relatively low pressures. Along with the upper

species, a new spectral pattern was recovered, specie X in figure 1. After careful inspection of the new spectral, it was assigned to the long sought after $\text{Rh}_4(\sigma\text{-CO})_{12}$.

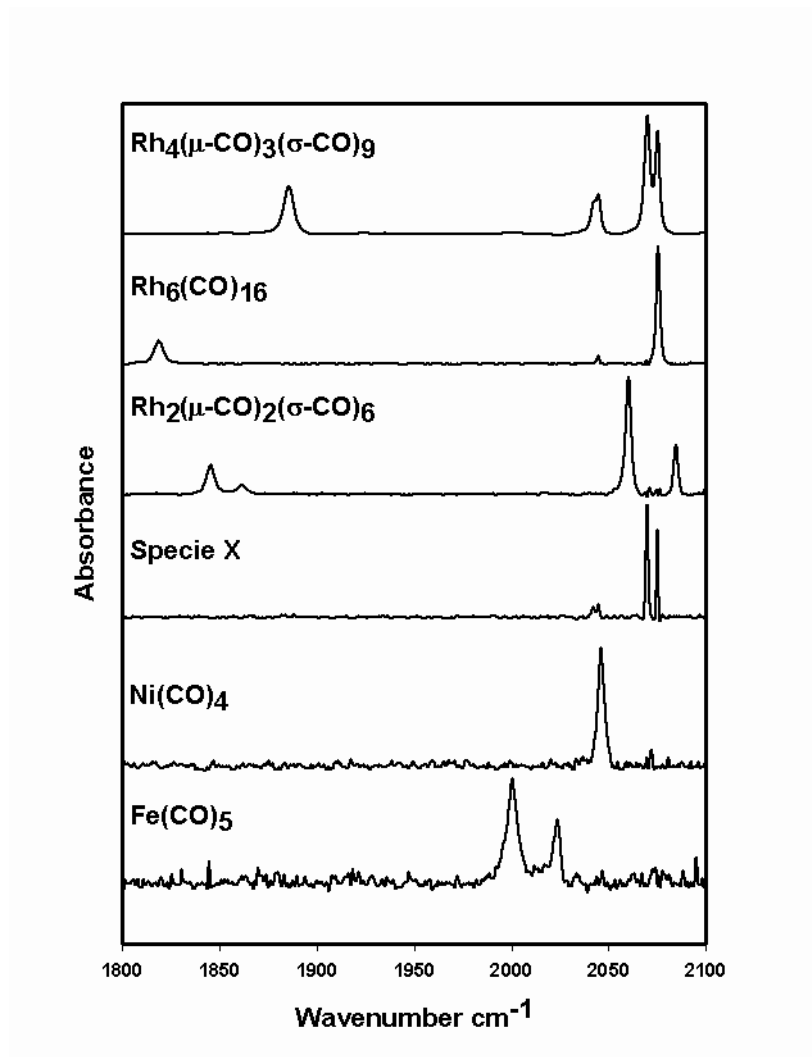


Figure 1. Pure component spectra obtained from BTEM analysis.

The normalized concentrations of the solutes are automatically provided by the BTEM analysis and are shown in figure 2.

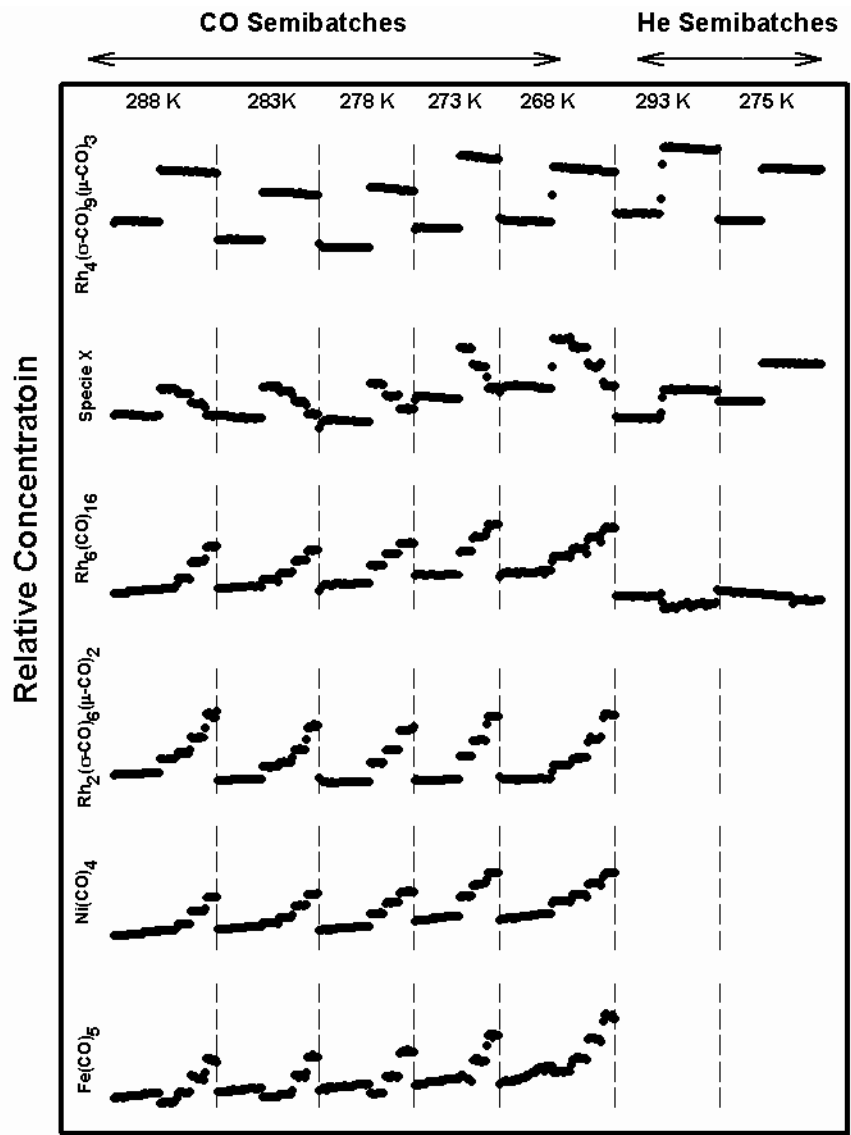


Figure 2. The normalized metal carbonyl concentrations provided by BTEM analysis for the 7 semibatch reactions.

Normalized concentration allows detailed explanation of each of species concentration profiles. In addition, comparison between the behavior of each specie under carbon monoxide versus Helium is made.

Rh₆(CO)₁₆ concentration increases with increasing CO pressure (purity 99.97%) due to the addition of impurities which promotes formation. On the other hand, the formation under high purity of Helium (99.9995) was not observed.

Rh₂(σ-CO)₆(μ-CO)₂ The equilibrated dinuclear complex Rh₂(σ-CO)₆(μ-CO)₂ increases as a function of CO pressure as anticipated¹³. However, under Helium the dinuclear complex Rh₂(σ-CO)₆(μ-CO)₂ is not formed since no excess CO is present. These observation is consistent with the Whyman's work with Rh₄(σ-CO)₉(μ-CO)₃ under CO and nitrogen¹³.

Impurities Ni(CO)₄ and Fe(CO)₅ increase with increasing CO pressure. The impurity Fe(CO)₅ is frequently present in commercial CO gas stored in steel cylinders, but this study is the first in which this group has been able to identify the presence of Ni(CO)₄. These impurities were not observed under Helium gas.

Real Concentrations and Equilibria. The data for the CO series of experiments were regressed to obtain the absolute (rather than L¹ normed) absorptivities for the four rhodium carbonyl clusters, namely, Rh₄(σ-CO)₉(μ-CO)₃, Rh₄(σ-CO)₁₂, Rh₂(σ-CO)₆(μ-CO)₂ and Rh₆(σ-CO)₁₂(μ₃-CO)₄. The mass balances for rhodium in each semibatch run, and each perturbation within the run, were used to constrain the numerical solutions. Details of similar optimization methods to properly scale absorptivities can be found elsewhere¹⁴.

The maximal absorptivities for Rh₄(σ-CO)₉(μ-CO)₃, Rh₄(σ-CO)₁₂, Rh₂(σ-CO)₆(μ-CO)₂ and Rh₆(σ-CO)₁₂(μ₃-CO)₄ were; 2.82 x 10⁴ l / mole cm (2070 cm⁻¹), 2.85 x 10⁵ l / mole cm (2069.8 cm⁻¹), 2.72 x 10⁴ l / mole cm (2060.2 cm⁻¹) and 1.34 x 10⁵ l / mole cm (2075.4 cm⁻¹) respectively. The absolute values for the absorptivities of Rh₄(σ-CO)₉(μ-CO)₃ and Rh₂(σ-CO)₆(μ-CO)₂ determined in this study are only marginally higher (circa 10%) than those previously determined in^{15,16}.

3.0 Conclusion

Using in situ high resolution FTIR coupled with BTEM enabled the identification, concentration and spectra, of minor species with concentration lower the 1 ppm with a great accuracy. The success of this study is very promising and prompted us to investigate more complex systems where species of interest have very low concentrations.

References

- ¹ F. A. Cotton, *Inorg. Chem.*, 5 (1966) 1083.
- ² F. A. Cotton, L. Kruczynski, J. Lewis, B. L. Shapiro, and L. F. Johnson, *J. Am. Chem. Soc.*, 94 (1972) 6191.
- ³ J. Evans, B. F. G. Johnson, J. Lewis, J. R. Norton, and F. A. Cotton, *J. Chem. Soc., Chem. Commun.*, 21 (1973) 807.
- ⁴ E. Band and E. L. Muetterties, *Chemical Reviews*, 78 (1978) 636.
- ⁵ Y. V. Roberts, B. F. Johnson and R. E. Benfield, *Inorganica Chimica Acta.*, 229 (1995) 221.
- ⁶ T. Eguchi and B. Heaton, *Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry*, 20 (1999) 3523.
- ⁷ C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, 89 (1967) 4792-3.
- ⁸ L. J. Farrugia, *Journal of Cluster Science*, 11 (2000) 39.
- ⁹ B. T. Heaton, L. Strona, R. Della Pergola, L. Garlaschelli, U. Sartorelli and I. H. Sadler, *J. Chem. Soc., Dalton Trans.*, (1983) 173.
- ¹⁰ W. Chew, E. Widjaja and M. Garland, *Organometallics*, 21 (2002) 1882.
- ¹¹ E. Widjaja, C. Li and M. Garland, *Organometallics*, 21 (2002) 1991-1997.
- ¹² C. Li, E. Widjaja, W. Chew and M. Garland, *Angewandte Chemie I.E.*, 20 (2002) 3785
- ¹³ R. Whyman, *J. Chem. Soc., Dalton Trans.* (1972) 1375
- ¹⁴ E. Widjaja, C. Li and M. Garland, *Journal of Catalysis*, 223 (2004) 278
- ¹⁵ M. Garland and P. Pino, *Organometallics*, 10 (1991) 16.
- ¹⁶ F. Oldani, G. Bor, *J. Organomet. Chem.*, 246 (1983) 309.