Investigation of the Reaction of $Rh_2(CO)_4Cl_2$ with 2,3-dimethyl-1,3-butadiene/isoprene by In-situ Vibrational Spectroscopies, BTEM Analysis and DFT Calculations

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Abstract—Reactions of $Rh_2(CO)_4Cl_2$ with two conjugated dienes, namely, 2,3-dimethyl-1,3-butadiene (DMBD) and isoprene, were performed in anhydrous hexane under argon atmosphere with multiple perturbations of reagents. These reactions were monitored by in-situ FTIR (FIR and MIR) and/or Raman spectroscopies and the collected spectra were further analyzed with BTEM family of algorithms. The combined spectroscopic data seems to suggest that one organo-rhodium product $Rh_2(CO)_4Cl_2(\eta^4\text{-diene})$ (diene = DMBD, isoprene) was the main product during the reactions. DFT calculations further confirm that three carbonyls are bonded to one rhodium atom while the 4th carbonyl and a chelating diene ligand are bonded to the other rhodium atom. The possible coordination geometry was obtained with (1) the consideration of the coordination chemistry and (2) the consistence between the DFT predicted spectra in FTIR and Raman regions with the corresponding BTEM estimates. The present contribution shows that BTEM can be meaningfully applied to the reaction of $Rh_2(CO)_4Cl_2$ and DMBD/isoprene in order to provide enhanced spectroscopic analysis, especially in the FIR and Raman regions. Furthermore, the present results provide a better understanding of the coordination chemistry of $Rh_2(CO)_4Cl_2$ with conjugated dienes.

Index Terms— Rhodium diene complexes; conjugated diene; in-situ spectroscopies; BTEM; DFT.

I. INTRODUCTION

Reactions of $Rh_2(CO)_4Cl_2$ with simple ligands (L) usually produce substituted dinuclear complexes $Rh_2(CO)_{4-m}Cl_2L_m$(m=1-4) as well as mononuclear complexes $Rh(CO)_{3-n}ClL_n$, (n= 1-3) [1-2]. These ligands include ethylene and phosphine etc. A cis-mononuclear complex $Rh(CO)_2Cl(py)$ was formed when pyridine(py) was used [3].

With respect to the rhodium complexes with conjugated dienes, Porri and Lionetti have reported some mononuclear bis(diene) complexes $[(diene)_2RhCl]$ (diene = butadiene, isoprene, trans-penta-l,3-diene, 2,3-dimethyl-butadiene, and

methyl hexa-2,4-dienoate) by reacting $RhCl_3$ with various dienes [4-5]. Some mixed mononuclear complexes $[(diene)(L)RhCl]$ (L = cyclooctene or p-toluidine) have also been reported by them with the similar method. In addition, two dinuclear complexes $[(diene)RhCl]_2$ (diene=2,3-dimethylbutadiene and cyclohexa-l,3-diene) have been prepared by reacting $RhCl_3$ with the dienes [6]. Dinuclear diene complexes $Rh_2(CO)_2Cl_2(COD)$ and $Rh_2Cl_2(COD)_2$ are the predominant species formed when $Rh_2(CO)_4Cl_2$ reacts with 1,5-cyclooctadiene (COD) [7-8]. An additional complex $Rh_2(CO)_4Cl_2(\eta^4\text{-}C_8H_{14})$ has also been reported when $Rh_2(CO)_4Cl_2$ reacted with 2,3-dimethyl-1,3-butadiene (DMBD). The proposed structure suggested that the diene ligand was acted as a bridge and the core structure was unchanged compared to the precursor $Rh_2(CO)_4Cl_2$ [9]. In general, a five-coordinated square pyramidal structure was preferred for the monnuclear complexes where the centers of the four C=C bonds constituting the basal plane and the chlorine atom occupying the apical position [10]. However, a four-coordinate, chlorine-bridged structure was preferred for the dinuclear complexes. In both mononuclear and dinuclear complexes, the diene ligand was found to be bonded to the rhodium atom in a chelate mode.

In-situ vibrational spectroscopes have been successfully used in combination with BTEM spectral analysis and DTF calculations to better understand the detailed chemistry of many organometallic and homogeneous catalyzed reactions, particular those involving rhodium carbonyl complexes [11-12]. In the present contribution, both FIR and low wavenumber MIR measurements are used, in addition to MIR and Raman in the carbonyl range, in order to better understand the coordination chemistry of conjugated dienes with $Rh_2(CO)_4Cl_2$. The BTEM analysis of the data provided the spectral estimates of two dinuclear rhodium complexes $Rh_2(CO)_4Cl_2(\eta^4\text{-diene})$ (diene = DMBD, isoprene) in various interest regions. DFT calculations were performed to explore the possible coordination geometries and predict their corresponding FTIR and Raman vibrational frequencies.

II. EXPERIMENTAL

General information All solution preparations and transfers were performed with Schlenk techniques [13] under argon (99.999%, Soxal, Singapore). The solvent hexane (99.6%+, Fluka) was refluxed for ca. 5 hours over

sodium-potassium alloy under argon. Rhodium carbonyl chloride (99%, Strem) 1,3-dimethyl-1,3-butadiene (99%, Sigma-Aldrich), and isoprene (99%, Sigma-Aldrich) were used as received.

Equipment setup and in-situ spectroscopic measurements A Bruker FTIR spectrometer (Vertex 70) with deuterated triglycine sulfate (DTGS) detector was used. The spectral resolution was 2 cm^{-1} for the MIR region of 400-5000 cm^{-1}. And the spectral resolution was 4 cm^{-1} for the FIR region of 30-700 cm^{-1}. A cell with diamond windows was used for the FIR measurements. Purified compressed air was used to purge the FTIR spectrometer system. In-situ Raman spectra in the region of 100-2400 cm^{-1} were recorded with a dispersive-type Raman microscope (InVia Reflex Renishaw, UK). The laser source used was a 785 nm near-infrared diode laser with 100% power (ca. 100 mW on the sample) and an exposure time of ca. 30 s. The in-situ spectroscopic measurements were performed at room temperature (ca. 24 ^{o}C).

The general experimental system has been reported elsewhere [11-12]. The reactions of Rh$_2$(CO)$_4$Cl$_2$ with DMBD/isoprene were performed under argon with multiple perturbations. A typical reaction was initiated by the injection of a certain amount of DMBD/isoprene solution through a rubber septum. Afterwards at pre-determined times, various perturbations of DMBD/isoprene solution and Rh$_2$(CO)$_4$Cl$_2$ powder were performed. It is well documented that multiple perturbation experiments greatly improve the quality of spectral reconstructions via BTEM.

Spectral reconstruction via BTEM family of algorithms Multi-reconstruction entropy minimization (MREM) [14-15] was used to first survey the underlying spectral patterns. Subsequently, based on the obtained initial local spectral estimates via MREM, the pure component spectral estimates were further refined using either BTEM [16-17] or tBTEM [18].

Density functional calculations Gaussian 09 [19] was used for all the calculations in this study. The geometric optimizations were performed using PBEPBE density function with DGDZVP basis set plus solvent effect of heptane and the FIR/MIR/Raman vibrational frequencies were calculated afterwards.

III. Results

Reactions of Rh$_2$(CO)$_4$Cl$_2$ with 2,3-dimethyl-1,3-butadiene (DMBD) The experimental spectra from the reaction of Rh$_2$(CO)$_4$Cl$_2$ with DMBD were cut into three regions, namely, 200-650, 800-1300, and 1500-2200 cm^{-1}, and further processed with the BTEM family of algorithms. The FIR/MIR BTEM estimates of Rh$_2$(CO)$_4$Cl$_2$(η^4-C$_8$H$_{14}$) in these three regions are shown in Fig. 1. Its corresponding FTIR-Raman BTEM estimate in the region of 1900-2150 cm^{-1} is shown in Fig. 2.

A combination of BTEM estimates of Rh$_2$(CO)$_4$Cl$_2$(η^2-C$_6$H$_{10}$) and DMBD and experimental reference of cell plus hexane and Rh$_2$(CO)$_4$Cl$_2$ in the carbonyl region of 1500-2200 cm^{-1} were used in the least squares fitting. The calculated relative concentrations are plotted in Fig. 3. Almost 100% signal recovery was obtained.
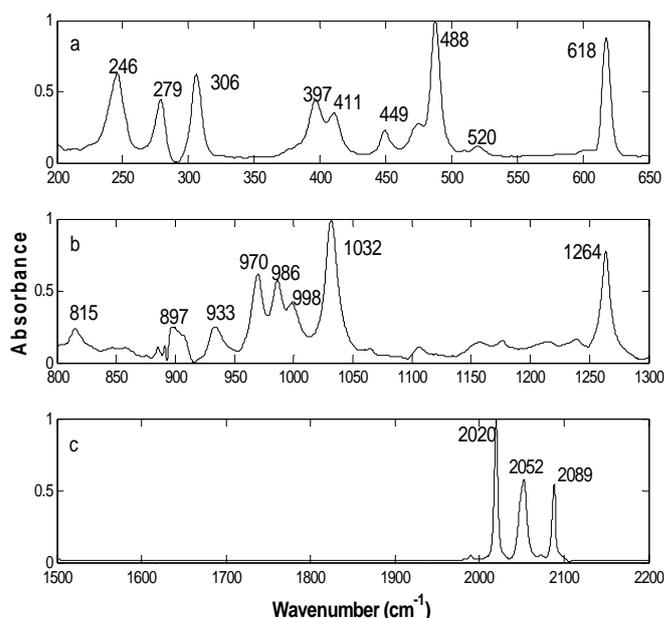
Fig. 1. The BTEM estimates of the organo-rhodium complex Rh$_2$(CO)$_4$Cl$_2$(η^4-C$_6$H$_{10}$) in the FIR/MIR region of (a) 200-650, (b) 800-1300, and (c) 1500-2200 cm^{-1}.
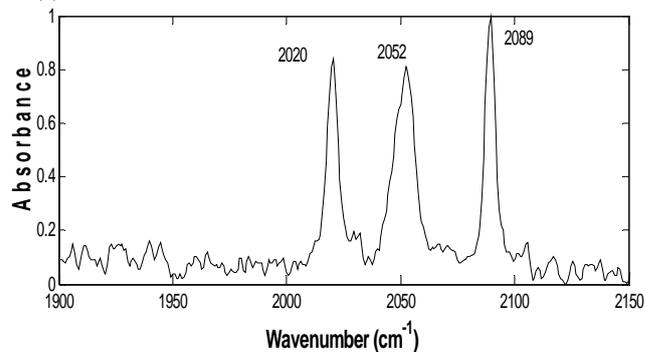
Fig. 2. The Raman BTEM estimate of Rh$_2$(CO)$_4$Cl$_2$(η^2-C$_6$H$_{10}$) in the region of 1900-2150 cm^{-1}.
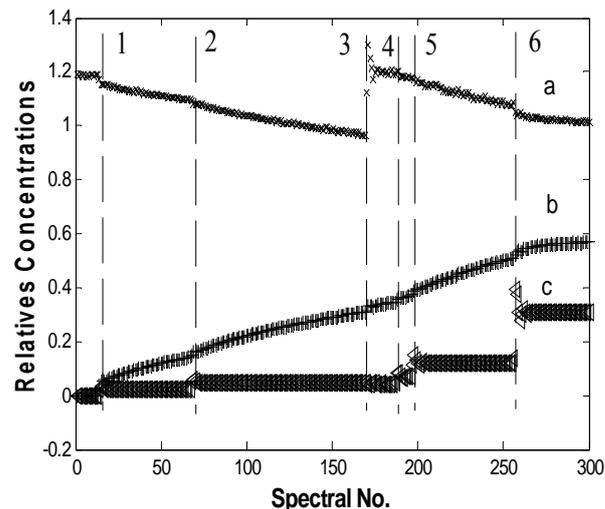
Fig. 3. The relative concentration profiles for the major species present in the system. (a) Rh$_2$(CO)$_4$Cl$_2$; (b) Rh$_2$(CO)$_4$Cl$_2$(η^4-C$_6$H$_{10}$); (c) DMBD. 1-2, 4. 20 μL DMBD injected in sequence; 3. 30 mg of Rh$_2$(CO)$_4$Cl$_2$; 5. 50 μL DMBD injected; 6. 200 μL DMBD injected.

Reactions of Rh$_2$(CO)$_4$Cl$_2$ with isoprene A similar spectral pattern was obtained when BTEM analysis was applied to the experimental spectra for the reaction of Rh$_2$(CO)$_4$Cl$_2$ with isoprene. The BTEM estimate of the organo-rhodium product Rh$_2$(CO)$_4$Cl$_2$(η^2-C$_5$H$_8$) in the MIR region of 1600-2200 cm^{-1} is plotted in Fig. 4. It should be noted here that one pure

component spectrum with maxima at 2016, 2054, 2061, and 2086 cm^{-1} was also recovered from the reaction of $Rh_2(CO)_4Cl_2$ with 1,5-cyclooctadiene (COD) although it was a minor species[20].
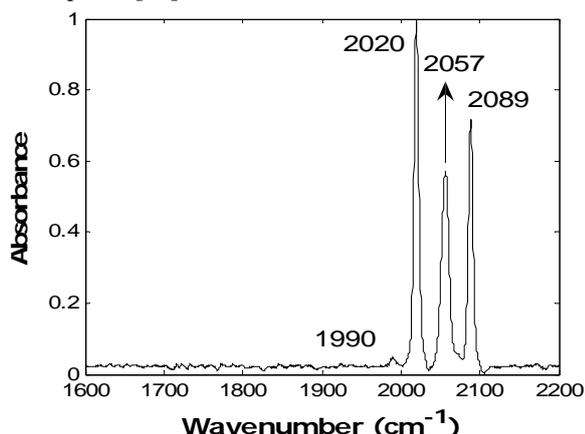
Fig. 4. The BTEM estimate of the organo-rhodium product $Rh_2(CO)_4Cl_2(\eta^2\text{-}C_5H_8)$ for the reaction of $Rh_2(CO)_4Cl_2$ with isoprene in the MIR region of 1600-2200 cm^{-1}.

DFT spectral prediction of $Rh_2(CO)_4Cl_2(\eta^4\text{-}C_6H_{10})$ The DFT predicted of $Rh_2(CO)_4Cl_2(\eta^4\text{-}C_6H_{10})$ in three FIR/MIR regions, namely, 200-650, 800-1300, and 1500-2200 cm^{-1}, are shown in Fig. 5. The corresponding Raman spectrum in the carbonyl region is shown in Fig. 6. It can be seen from this figure that the DFT predicted and the BTEM estimated wavenumbers (Figs. 1 and 2) show a systematic deviation of 0-2% in the MIR region and ca. 1-10% in the FIR region. Therefore the DFT predicted spectra are fairly consistent with the BTEM estimates in the three regions.
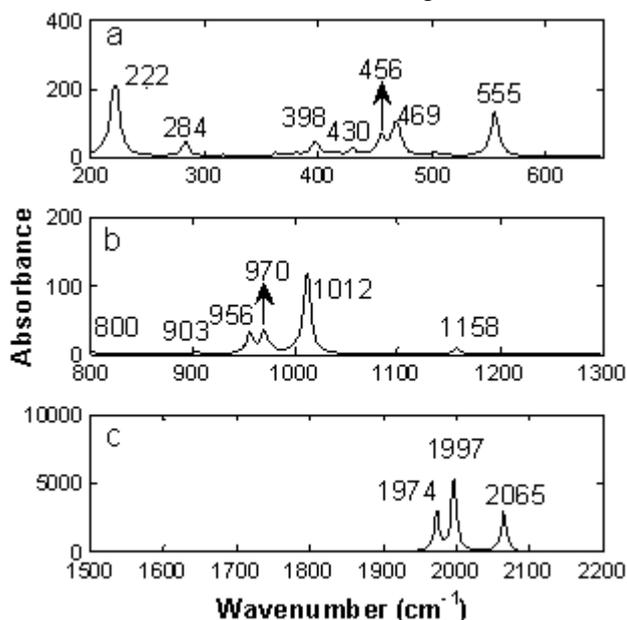
Fig. 5. The DFT predicted spectra of $Rh_2(CO)_4Cl_2(\eta^4\text{-}C_6H_{10})$ in three FIR/MIR regions. (a) 200-650, (b) 800-1300, and (c) 1500-2200 cm^{-1}.

The optimized geometry of $Rh_2(CO)_4Cl_2(\eta^4\text{-}C_6H_{10})$ is plotted in Fig. 7. The core structure consists of two Rh atoms bridged by two Cl atoms. This core structure is obviously non-planar, the dihedral angle about the Cl⋯Cl hinge is ca. 141° which is larger than that of $Rh_2(CO)_4Cl_2$ (ca. 124°). Three carbonyls are bonded to one rhodium atom while the 4th carbonyl and a chelating diene ligand are bonded to the other rhodium atom.

In addition, the DFT predicted wavenumbers (2001 and 2059 cm^{-1}) of the bridged-diene species are similar to those of the precursor $Rh_2(CO)_4Cl_2$ (2003 and 2060 cm^{-1}). This similarity may arise from the similar core structures of these two species.
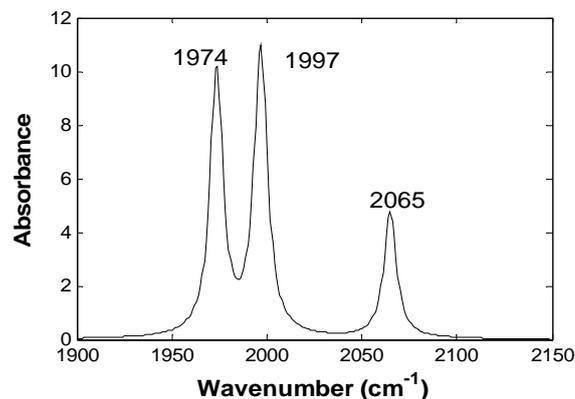
Fig. 6. The DFT predicted Raman spectrum of $Rh_2(CO)_4Cl_2(\eta^4\text{-}C_6H_{10})$ in the carbonyl region of 1900-2150 cm^{-1}.
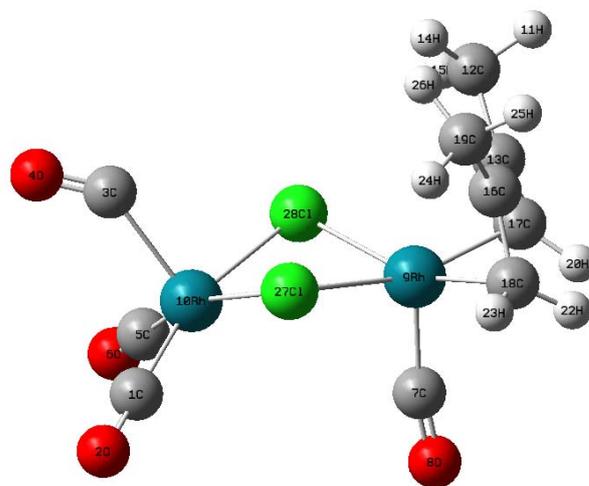
Fig. 7. The optimized geometry of $Rh_2(CO)_4Cl_2(\eta^4\text{-}C_7H_{12})$.

DFT spectral prediction of $Rh_2(CO)_4Cl_2(\eta^4\text{-}C_5H_8)$ The DFT predicted spectrum of $Rh_2(CO)_4Cl_2(\eta^4\text{-}C_5H_8)$ in the carbonyl region is shown in Fig. 8. A systematic deviation (0-2%) from the BTEM estimated frequencies (Fig. 4) was also observed in the carbonyl region. It is worthwhile to mention here that the predicted frequencies and optimized geometry of $Rh_2(CO)_4Cl_2(\eta^4\text{-}C_5H_8)$ are similar to those of $Rh_2(CO)_4Cl_2(\eta^4\text{-}C_6H_{10})$.
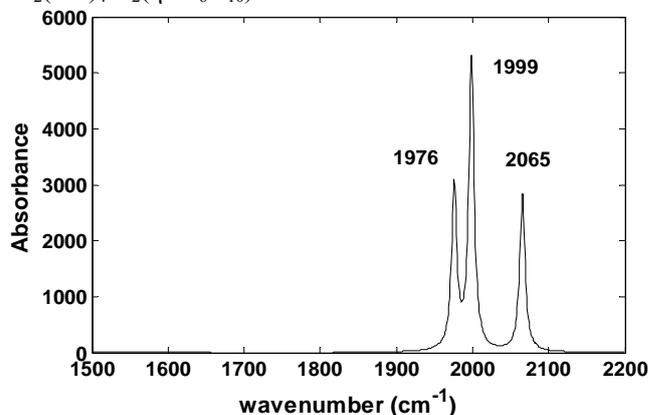
Fig. 8. The DFT predicted spectrum of $Rh_2(CO)_4Cl_2(\eta^4\text{-}C_5H_8)$ in the carbonyl regions of 1900-2150 cm^{-1}.

IV. Discussion

In-situ FTIR and/or Raman measurements were combined with signal processing and DFT calculations in order to better understand the reactions of $Rh_2(CO)_4Cl_2$ with DMBD and isoprene. The major species formed was a known diene complex $Rh_2(CO)_4Cl_2(\eta^4\text{-diene})$ (diene = DMBD, isoprene). The carbonyl band pattern shown in Figs. 1c, 2 and 4 suggest that the species may be a dinuclear with low symmetry and four carbonyl ligands. DFT calculations further confirm that the possible structure of this dinuclear species may be with three carbonyls bonded to one Rh atom and the 4th carbonyl and a chelating diene ligand bonded to the other Rh atom. And the two Rh atoms are bridged by two Cl atoms. This assignment was made based on the consistency between the DFT predicted spectra and the BTEM estimates, as well as consideration of the potential coordination chemistry.

Differences were observed between the DFT predicted wavenumbers and the BTEM estimates for the major organo-rhodium species. These differences may be due to the difficulties to accurately model the electron density associated with the Rh-Cl, Rh-Rh and Rh-C bonds.

V. Conclusion

A combination of in-situ FTIR and/or Raman spectroscopic measurements, BTEM reconstruction and DFT calculations was successfully used to study the reactions of $Rh_2(CO)_4Cl_2$ with DMBD and isoprene. One known organo-rhodium complex $Rh_2(CO)_4Cl_2(\eta^2\text{-}C_6H_{10})$ was formed as the primary species. The pure component spectra of $Rh_2(CO)_4Cl_2(\eta^4\text{-}C_6H_{10})$ in the FIR (200-650 cm^{-1}) and MIR (800-1300 and 1500-2200 cm^{-1}) regions were successfully recovered with the application of BTEM family of algorithms and without the purification from the solution. This study demonstrate that with the combination of in-situ spectroscopic study, BTEM reconstruction and DFT calculations, some of the diverse and complex coordination chemistries between $Rh_2(CO)_4Cl_2$ and conjugated dienes can be addressed.

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