

Temperature Dependent Rh···Rh EXAFS in Dinuclear and Adsorbed Rhodium Species

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EXAFS (extended X-ray absorption fine structure) spectroscopy has become an important tool for the characterization of heterogeneous and supported metal catalysts.¹ The information obtained from EXAFS data is of three types: backscatterer identity (i.e., atomic number) for the atoms in the local environment of the absorber; absorber–backscatterer distances; and the number of backscatterer atoms of a certain type (the coordination number, CN) within a shell around the absorbing atom. One of the most important pieces of information which may be obtained from EXAFS studies of supported metal catalysts is the number of metal atoms in the local environment of the X-ray absorbing atom. From these data, models for the degree of aggregation have frequently been proposed.² In a recent study of metal adsorbates,³ we have observed in several model complexes that EXAFS absorber–backscatterer features for metal–metal interactions may be highly temperature dependent. This in turn can make metal–metal EXAFS undetectable in data collected at room temperature. The importance of observing these features in order to correctly identify adsorbate species in heterogeneous catalyst systems cannot be overemphasized and prompts us to give a preliminary account of our results on crystallographically characterized Rh complexes.

The well-known dimeric, rhodium complexes (RhL)₂(μ-X)₂ (X = Cl, L = (C₂H₄)₂ (1);³ L = cyclooctadiene (cod) (2);³ L = (CO)₂ (3);⁴ X = OH, L = cod (4)⁵) serve as precursors to many homogeneous and heterogeneous catalysts.⁶ The rhodium EXAFS of 1 is particularly well suited for variable temperature analysis. On the basis of the crystal structure,⁷ three well-separated features are expected in Fourier transforms (FTs) of the data: a Rh···Rh feature (CN = 1) at approximately 3.1 Å, a Rh–Cl feature (CN = 2) at approximately 2.4 Å, and a Rh–C feature (CN = 4) at 1.9 Å. Figure 1a illustrates the FTs for 1 at temperatures between 4 and 300 K.^{8–10} At low

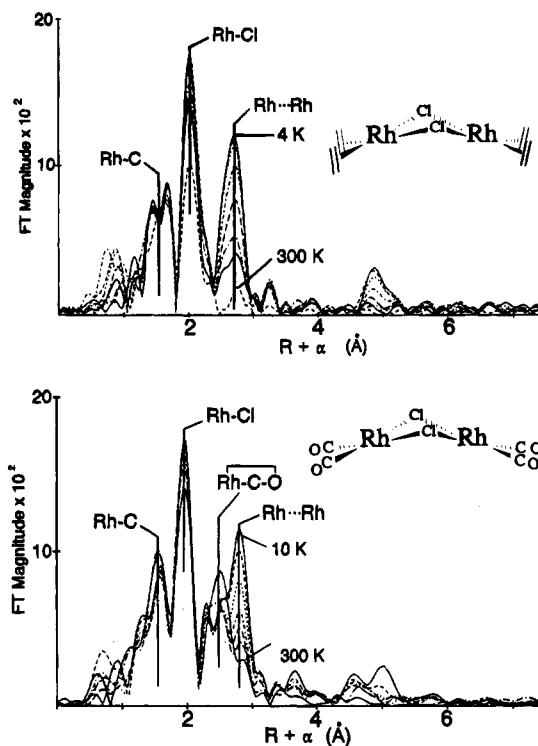


Figure 1. (a, top) Overlying FT plots of EXAFS for [Rh(μ-Cl)(C₂H₄)₂]₂ for temperatures between 4 and 300 K. Intermediate unlabeled temperatures are 10, 35, 70, 100, 150, and 200 K. (b, bottom) Overlying FT plots of EXAFS for [Rh(μ-Cl)(CO)₂]₂ for temperatures between 10 and 300 K. Intermediate unlabeled temperatures are 44, 78, 112, 146, and 180 K. The FT range for both is (3–17) Å. The ordinate axes are uncorrected for EXAFS phase shifts (α), which causes all features on the R + α scale to be ca. 0.4 Å less than the true distances associated with these features. Apparent splitting of the R–C feature in part a and the RhC=O feature in part b is due to nonlinearities in the EXAFS phase when the data are extended to k = 17 Å⁻¹.

temperature (*T* < 10 K) three prominent features are observed. Analysis of these data are consistent with the known structure and the expectations described above. Upon warming of the sample, the Rh···Rh feature shows a significant decrease until it disappears into the noise at 300 K. The Rh–Cl feature in the FTs shows a much smaller decrease in intensity compared to the Rh···Rh feature, and the Rh–C feature appears to be largely unaffected over the same temperature range. Similar behavior is observed for 2 although the Rh···Rh feature does not completely disappear at 300 K. Figure 1b shows the FTs for the carbonyl complex 3. Two earlier EXAFS studies of this complex, one at room temperature¹¹ and one at 77 K,¹² attributed the feature at R + α = 2.6 Å to Rh···O_{carbonyl} EXAFS and failed to recognize a Rh···Rh contribution to this peak. The intensity of the Rh···O feature of the Rh–CO moiety is significantly enhanced due to multiple scattering and at room temperature dominates the Rh···Rh feature. At low temperature, however, the opposite is observed, with the Rh···Rh feature dominating the EXAFS within this shell.

(9) Analysis of EXAFS followed standard procedures and utilized the XFPACK data reduction package. Both theoretical (FEFF6)¹⁰ and empirical parameters (lowest temperature data for each neat sample) were used for EXAFS amplitude and phase functions. A full description of single and multiple scattering contributions to the models for the data for these samples will be presented in a full paper (manuscript in preparation).

(10) Rehr, J. J.; Zabinsky, S. I.; Albers, R. D. *Phys. Rev. Lett.* **1992**, *69*, 3397.

(11) Asakura, K.; Kitamura-Bando, K.; Iwasawa, Y.; Arakawa, H.; Isobe, K. *J. Am. Chem. Soc.* **1990**, *112*, 9096.

(12) van't Blik, H. F. J.; van Zon, J. B. A. D.; Huizinga, T.; Vis, J. C.; Koningsberger, D. C.; Prins, R. *J. Am. Chem. Soc.* **1985**, *107*, 3139.

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(1) Bertognolli, H.; Ertel, T. S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 45–66.

(2) Sinfelt, J. H.; Via, G. H.; Lytle, F. W. *Catal. Rev. Sci. Eng.* **1984**, *26*, 81. Bart, J. C. J.; Vlaic, G. *Adv. Catal.* **1987**, *35*, 1. Asakura, K.; Iwasawa, Y. *J. Phys. Chem.* **1989**, *93*, 4213.

(3) Vierkötter, S. A.; Barnes, C. E.; Hatmaker, T. L.; Penner-Hahn, J. E.; Stinson, C. M.; Huggins, B. A.; Benesi, A.; Ellis, P. D. *Organometallics* **1991**, *10*, 3803.

(4) Walz, L.; Scheer, P. *Acta Crystallogr.* **1991**, *C47*, 640.

(5) Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1983**, *23*, 126.

(6) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(7) Vierkötter, S. A.; Barnes, C. E.; Garner, G. L.; Butler, L. G. *J. Am. Chem. Soc.* **1994**, *116*, 7445.

(8) Rh K-edge (23.220 keV) EXAFS experiments were performed on the X-ray stations 4-3 and 7-1 at the Stanford Synchrotron Radiation Laboratory (SSRL) (ring energy, 3 GeV; ring current between 100 and 40 mA) using a Si[220] monochromator, detuned 30% for harmonic rejection. Measurements were made in the transmission mode using Ar ion chambers and a He flow cryostat (Oxford CF-1204).

This behavior is exhibited by all the complexes introduced above: *all Rh···Rh components in the EXAFS for complexes 1–4 show a decrease in intensity as the temperature approaches 300 K. In most cases the Rh···Rh feature in FTs of the data is so weak at 300 K that its detection above background noise is difficult and quantitative analysis of this feature is impossible.* These observations clearly illustrate the necessity for collecting EXAFS data at low temperature in order to minimize thermal disorder and to be able to observe all absorber–scatterer components in the data, especially ones derived from metal–metal scattering pairs.

When EXAFS data are fitted for an unknown backscatterer environment, typically both the coordination number (CN) and Debye–Waller factor (σ^2) are refinement parameters together with absorber–backscatterer separation. In practice, although σ^2 and CN are usually highly correlated, it is generally possible to determine CN values to $\pm 25\%$. When both the CN and σ^2 are refined for 1–4, reasonable values for the coordination number were obtained only at low temperature.¹³ In particular, the apparent coordination numbers decreased steadily as the temperature was raised until the feature became so weak that it could no longer be modeled successfully.

It is clear that the thermal disorder must be increasing rather than CN decreasing. The failure of CN to refine to a value near 1 for temperatures greater than 150 K most likely reflects the presence of significant anharmonicity in the Rh···Rh pair distribution function.¹⁴ That is, the simple Gaussian model for σ^2 is not adequate for the distortion at higher temperatures. Since the coordination number is 1 at all temperatures, we can constrain this parameter. In this case, reasonable EXAFS fits are obtained and σ^2 increases monotonically with temperature. If the CN were not known, it would not be possible to determine it correctly for temperatures greater than 150 K.

The pronounced temperature dependence for 1–4 is surprising. It is well-known that EXAFS amplitudes are temperature dependent due to dynamic disorder contributions to the Debye–Waller factor, σ^2 . What is unusual is that the dynamic disorder can be so pronounced as to render some interactions nondetectable while the crystal structures of 1–3 show no evidence for unusual thermal motion in the solid state.¹⁵ The solution to this apparent paradox can be seen if the crystallographic temperature factors are used to calculate the expected EXAFS

(13) Refined CNs of approximately 1.0 were obtained for 4 and 10 K data for all complexes. At 200 K, refined values for the CN for the Rh–Rh feature for 1 and 2 were 0.63 and 0.54. In most cases, the Rh–Rh feature could not be modeled successfully with room temperature data. DW factors were also found to differ appreciably between analyses where the coordination number was fixed or refined on.

(14) Bunker, G. *Nucl. Instrum. Methods* **1983**, 207, 437.

(15) The thermal ellipsoids for the Rh and Cl atoms are all normal ($U_{iso} < 5 \times 10^{-2} \text{ \AA}^2$) and reasonably isotropic.

σ^2 . If the Rh···Rh motion is assumed to be completely uncorrelated, the EXAFS σ^2 is simply the sum of the σ^2_{atomic} for each Rh. From the crystallographic data at room temperature, this gives $\sigma^2 \approx 0.1 \text{ \AA}^2$. This is sufficiently large as to make the Rh···Rh EXAFS unobservable. The observation that Rh···Rh EXAFS nevertheless appears at low temperature indicates that, at sufficiently low temperature, the Rh···Rh motion must become highly correlated.

Adsorption of complexes 1–3 onto dehydrated alumina leads to fragmentation of the Rh₂Cl₂ core and replacement of most Rh–Cl bonds with Rh–O bonds to surface functionality.³ In no instance, either at high or low temperature, was a Rh···Rh feature observed for the adsorbed species. Different results are observed when the hydroxy-bridged complex 4 is adsorbed onto alumina.¹⁶ At low temperature a strong Rh···Rh feature is observed in the FTs, indicating that the dimer remains intact on the surface. If only room temperature data had been collected, this feature would have been difficult to observe or missed entirely. The above examples illustrate how room temperature data alone can lead to misinterpretations of the EXAFS data and ultimately to misidentification of adsorbate species.

In conclusion, the preliminary results of our study on a series of dinuclear rhodium model complexes and resulting adsorbed species indicate that the observation of metal–metal EXAFS can be highly temperature dependent and missing in room temperature data. For metal adsorbates, where bridged polynuclear species are possible surface species, observation of metal–metal EXAFS is critical in correctly identifying adsorbed species, and thus the collection and analysis of low temperature data is imperative. Room temperature data can lead to low apparent coordination numbers. Our current work is directed toward a more quantitative analysis of the temperature dependence of the Debye–Waller factor and a broader survey of the occurrence of these temperature effects in EXAFS data.

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(16) Vierkötter, S. A. Ph.D. Thesis, Department of Chemistry, University of Tennessee, May 1994. Ralle, M.; Barnes, C. E.; Vierkötter, S. A.; Clark, K.; Penner-Hahn, J. E. Manuscript in preparation.