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Structure of the Catalytic Site of Polymer-Bound Wilkinson's Catalyst by X-Ray Absorption Studies

Sir:

Recently, there has been considerable interest in linking homogeneous catalysis to heterogeneous catalysis by using insoluble organic polymers as supports for transition metal catalysts.¹ Polymer-bound Wilkinson's catalyst,² $(\text{Ph}_3\text{P})_3\text{-RhCl}$, has been investigated³ as a hydrogenation catalyst where the supporting medium is polystyrene cross-linked with divinylbenzene. Despite Collman et al.'s⁴ work on RhClL_3 (where L = cross-linked polystyrene-*p*- C_6H_4 - PPh_2), the detailed structures of these heterogenized homogeneous catalysts⁵ remain essentially unknown.

We report herein the interatomic distances and coordination of Wilkinson's catalyst (red isomer,^{2,6} **1**), polymer-bound Wilkinson's catalyst³ (**2**), and hydrogenated polymer-bound Wilkinson's catalyst⁷ (**3**) as determined by x-ray absorption studies performed with synchrotron radiation at the Stanford Synchrotron Radiation Project.⁸⁻¹³ This technique has been used to measure internuclear distances in iron-sulfur proteins,¹⁴ copper salts in aqueous solutions,¹² and various molecules.^{15,16}

It has been shown,¹⁷⁻²² that the modulation $\Delta\mu$ of the x-ray absorption coefficient of an atom is given by

$$\chi(k) = \frac{\Delta\mu}{\mu} = \sum_j \frac{-N_j |f_j(k, \pi)| e^{-2\sigma_j^2 k^2}}{R_j^2 k} \sin [2kR_j + \phi_j(k)] \quad (1)$$

where N_j is the number of scattering atoms j at a distance R_j to the absorbing atom with a Debye-Waller-like factor $e^{-2\sigma_j^2 k^2}$.²³ The $\phi_j(k)$ and $f_j(k, \pi)$ are energy-dependent phase-shift and electron back-scattering form factor. The k wave vector of the emitted photoelectron is given by

$$k = \sqrt{2m(E - E_{\text{th}})/\hbar^2} \quad (2)$$

where E_{th} is the absorption threshold energy for the atom. $\phi_j(k)$ depends upon the absorbing and the neighboring atoms whereas $f_j(k, \pi)$ depends only on the neighboring atom j .¹⁹ Thus, above threshold, one observes (Figure 1) a sinusoidal variation of the x-ray absorption in which the frequency depends on R_j and $\phi_j(k)$ and the amplitude depends on N_j , σ_j , and $f_j(k, \pi)$. In this work, we used model compounds $\text{Rh}(\text{dppe})_2^+$ (dppe, diphenylphosphinoethane) and $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ to obtain $\phi_j(k)$ and $f_j(k, \pi)$ for Rh-P and Rh-Cl bonds.^{19,24} To determine N_j and R_j for **1**, **2**, and **3** the Fourier filtered data which included only nearest neighbor contributions (the only predominant feature in the Fourier transform) were fitted to the function

$$\frac{\Delta\mu}{\mu} = N_{\text{P}_1} \sin [2kR_{\text{P}_1} + \phi_{\text{P}_1}(k)] f_{\text{P}_1}(k) e^{-2\sigma_{\text{P}_1}^2 k^2} + N_{\text{P}_2} \sin [2kR_{\text{P}_2} + \phi_{\text{P}_2}(k)] f_{\text{P}_2}(k) e^{-2\sigma_{\text{P}_2}^2 k^2} + N_{\text{Cl}} \sin [2kR_{\text{Cl}} + \phi_{\text{Cl}}(k)] f_{\text{Cl}}(k) e^{-2\sigma_{\text{Cl}}^2 k^2} \quad (3)$$

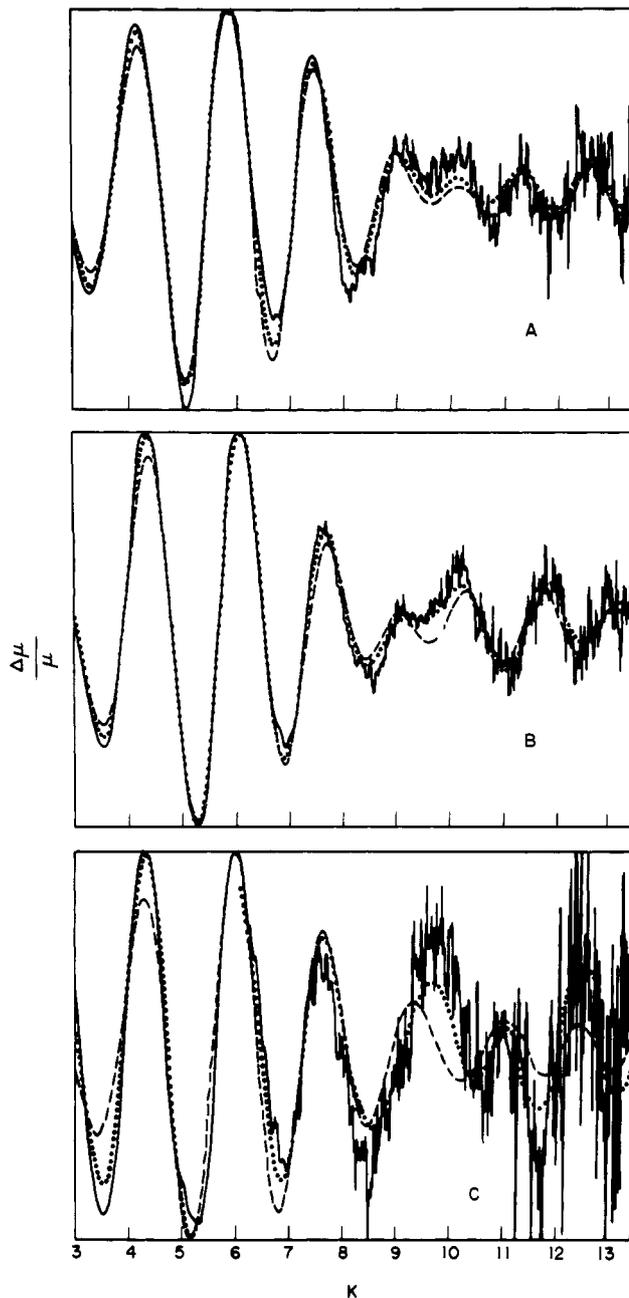


Figure 1. Raw (—), Fourier filtered (···) and fit (---) of data, multiplied by k^3 : A, $(\text{PPh}_3)_3\text{RhCl}$; B, polymer-bound $(\text{PPh}_3)_3\text{RhCl}$; C, hydrogenated polymer-bound $(\text{PPh}_3)_3\text{RhCl}$.

The results of the fitting procedure are summarized in Table I. The significant phase shift difference (~ 0.5 rad) between $\phi_{\text{P}}(k)$ and $\phi_{\text{Cl}}(k)$ enables one to distinguish between phosphorus and chlorine contributions.¹⁹ This fitting technique²⁴ also gave information about the number of phosphorus vs. chlorine (scatterers) atoms attached to the rhodium (absorber) atom. In Figure 2 the sum of the squares of the fit residuals (χ^2) is plotted for several values of $N_{\text{P}} = N_{\text{P}_1} + N_{\text{P}_2}$ and N_{Cl} . In this fit of the data only integral N_{P_1} , N_{P_2} , and N_{Cl} values were considered.

The interatomic distances (cf. Table I) in **1** are: Rh-Cl, 2.35, one short Rh-P₁ of 2.23, and two long Rh-P₂ of 2.35 Å, which are in agreement with those determined by x-ray crystallography.⁶ Furthermore, our result (cf. curve A in Figure 2) clearly shows that the best fit occurs at P:Cl ratio of 3:1 (viz., 1:2:1 $N_{\text{P}_1}:N_{\text{P}_2}:N_{\text{Cl}}$).

The distances found for **2** showed the loss of the two long

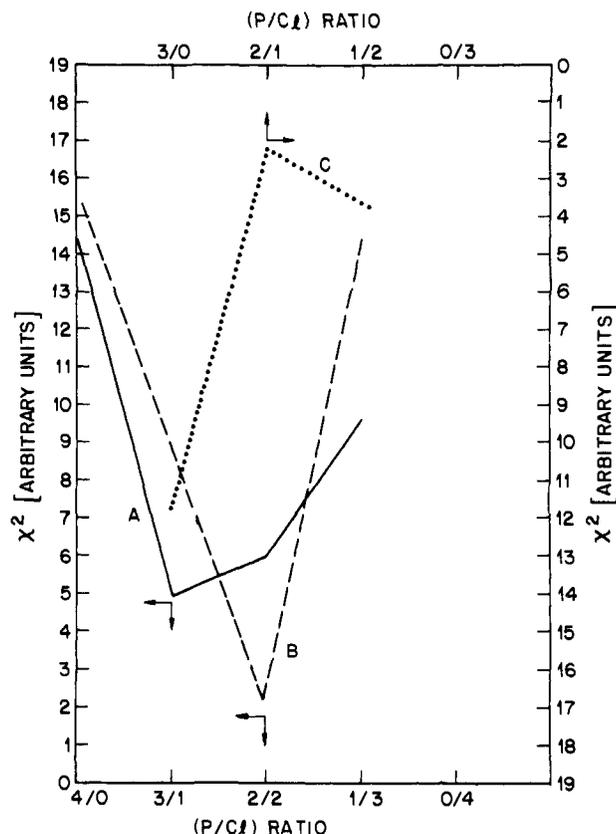
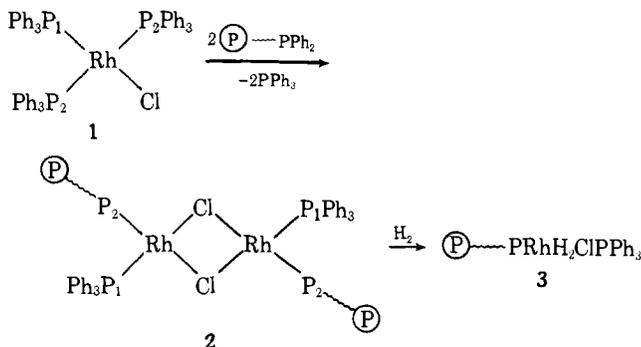


Figure 2. Plot of χ^2 (sum of squares of residuals) vs. P:Cl ratio. χ^2 minimum occurs at a P:Cl ratio of 3:1 for **1** (curve A), 2:2 for **2** (curve B), and 2:1 for **3** (curve C).

Rh-P bonds of 2.35 (1) Å and the formation of a new short Rh-P₂ distance of 2.16 Å which may be assigned to the phosphorus attached to the polymer. The analysis of the coordination numbers for **2** shows the best fit of the data at P:Cl ratio of 2:2 (viz., 1:1:2 $N_{P_1}:N_{P_2}:N_{Cl}$) (cf. Figure 2). For Rh(I), this can only be achieved through dimerization.

The polymer-bound catalyst **2** undergoes an oxidative addition reaction with H₂ to give a Rh(III) species **3**. Our results (Table I) indicate that the chloride bridges in **2** are cleaved to form **3** upon hydrogenation, with two phosphorus and one chlorine atoms around the rhodium (i.e., 1:1:1 $N_{P_1}:N_{P_2}:N_{Cl}$; see Figure 2C). The fit obtained for this system was not nearly so good as for **1** and **2** which leads us to conclude that the oxidative addition reaction was probably not complete.

Based on the above observations, we propose the following scheme for the structural changes at the active sites of the polymer-bound catalysts.



The present study of polymer-bound Wilkinson's catalyst (**2**) suggests that the catalyst can aggregate to form binuclear

Table I. Summary of Interatomic Distances^a

	Wilkinson's 1		Polymer-bound Wilkinson's 2	Hydrogenated polymer-bound Wilkinson's 3
	X-ray ^b	EXAFS		
Rh-Cl	2.376 [1] ^c	2.35 (1) ^d	[2] ^c 2.33 (1) ^d	[1] ^c 2.29 (1) ^d
Rh-P ₁	2.214 [1]	2.23 (1)	[1] 2.23 (1)	[1] 2.20 (1)
Rh-P ₂	2.326 [2]	2.35 (1)	[1] 2.16 (1)	[1] 2.38 (1)

^a Reference 24. ^b Reference 6. ^c Number of bonds of this type. ^d The numbers in parentheses are the \pm variation in the distance determination which produce a doubling of the χ^2 obtained from fitting if one allows the other parameters to change. These values are probably underestimated by a factor of two when systematic errors such as background removal, Fourier filtering are included.

clusters when attached to a polymer. This is consistent with the observations that selective hydrogenations occur at slower rates in polymer-bound catalyst.¹⁸ However, it is suggested that the dimeric structure found for **2** could be a function of the method of preparation and the degree of cross-linking.²⁰

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