Structure of Bromotris(triphenylphosphine)rhodium(I) by Extended *X*-Ray Absorption Fine Structure (EXAFS)

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Summary The previously unknown interatomic bond distances and co-ordination geometry of bromotris-(triphenylphosphine)rhodium(I), [RhBr(PPh_3)$_3$], have been determined by a new structural technique, extended *X*-ray absorption fine structure.

THE new analysis technique, extended *X*-ray absorption fine structure (EXAFS), has been used to determine interatomic distances in iron–sulphur proteins,[1] copper salts in aqueous solutions,[2] and a polymer-bound rhodium(I) catalyst.[3] We report here determination of the interatomic bond distances and co-ordination of bromotris(triphenylphosphine)rhodium(I) by EXAFS. Structural data for this complex have not been reported, although the structure of the chloro-analogue[4] (Wilkinson's catalyst) has been determined.[5,6] There appears to be only one report of a structure in which an Rh^I–Br distance has been determined.[7] The catalytic activities of [RhX(PPh_3)$_3$], where X = Cl or Br, are expected to be similar, suggesting the need for structural data on rhodium(I) systems containing bromine and phosphine ligands.[8]

The EXAFS experiments were performed with synchrotron radiation at the Stanford Synchrotron Radiation Project.[9] The current theoretical view of EXAFS[10] is that the modulation of the *X*-ray absorption coefficient, $\chi = (\mu - \mu_0)/\mu_0$, is due to interference between the back-scattered and outgoing photoelectrons in the photo-absorption matrix element, where μ_0 is the absorption coefficient of an isolated atom. Thus, the modulation

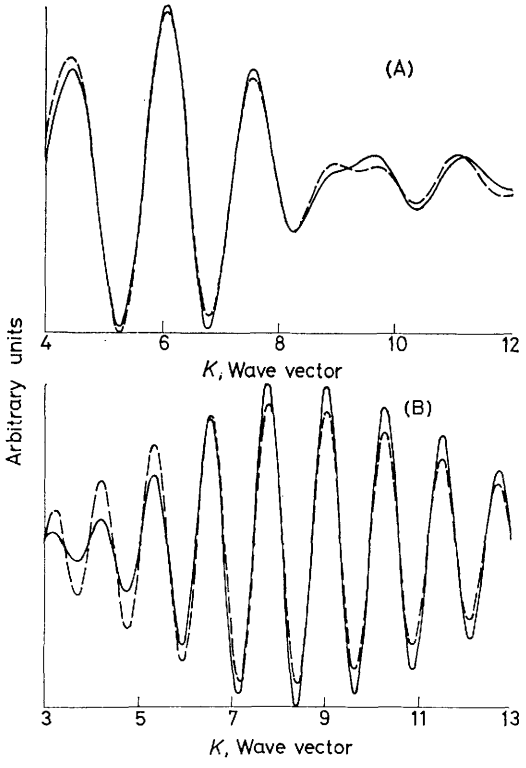

FIGURE 1. Fitting results: (A) the Rh-EXAFS in [RhBr(PPh_3)$_3$]; (B) the Br-EXAFS in [RhBr(PPh_3)$_3$]; solid lines, experimental data; broken lines, fit.

$\Delta\mu/\mu$, of the X-ray absorption coefficient of an atom is given by equation (1), where N_j is the number of scattering

$$\Delta\mu/\mu = \sum_j N_j |f_j(k,\pi)| \exp(-2\sigma_j^2 k^2) \sin[2kR_j + \phi_j(k)]/R_j^2 k \quad (1)$$

atoms j at a distance R_j from the absorbing atom with a Debye–Waller like factor of $\exp(-2\sigma_j^2 k^2)$.

The $\phi_j(k)$ and $f_j(k,\pi)$ terms are energy-dependent phase shifts and amplitude functions for the scatterers respectively and k is the wave vector of the emitted photoelectron.

In the data analysis,[11] theoretical phase shifts and amplitudes were used to fit the data to equation (1) and the measured EXAFS for Rh and Br in $[RhBr(PPh_3)_3]$ (Figure 1). The Fourier transforms of the data in Figure 2 show that for the Rh-EXAFS in $[RhBr(PPh_3)_3]$, there are two peaks, Rh–P and Rh–Br, indicative of multiple distances. In the Br-EXAFS the Br sees only the rhodium atom as a nearest neighbour, thus giving rise to a single frequency, and hence a single peak and distance in the analysis.

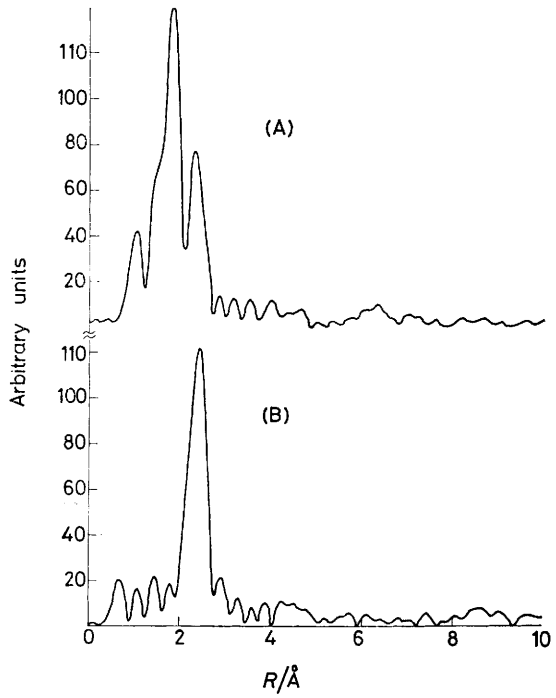

FIGURE 2. (A) Fourier transform of the Rh-EXAFS in $[RhBr(PPh_3)_3]$; (B) Fourier transform of the Br-EXAFS in $[RhBr(PPh_3)_3]$.

We have, therefore, two independent results with which to confirm the Rh–Br distance. The results of fitting the Rh-EXAFS and Br-EXAFS data for $[RhBr(PPh_3)_3]$ are shown in Table 1. The results gave three distinct determinations of the Rh–Br distances, two of which were obtained from independent experiments and a third from an empirical data analysis program. The Rh–Br distances were 2·540, 2·535, and 2·536 Å.

TABLE 1. Interatomic distance in $[RhBr(PPh_3)_3]_3$ by analysis of the Rh-EXAFS and Br-EXAFS

	Rh-EXAFS	Br-EXAFS	
	Method 1[a]	Method 1	Method 2
Rh–Br	[1][b] 2·540 (8)	2·536 (8)	2·535 (8)
Ph–P(1)	[1] 2·18 (1)	—	—
Rh–P(2)	[2] 2·31 (1)	—	—

[a] Method 1, fitted function, equation (1); Method 2, empirical method. [b] Number of bonds of this type.

The Rh–P distances were 2·18 and 2·31 Å, which were determined by fitting the Rh-EXAFS data with theoretical Rh–P and Rh–Br phase shifts and amplitudes.

The fitting technique also gave information about the co-ordination number of atoms attached to the rhodium (absorber) atom. In Figure 3 the sum of the squares of the fit residuals (χ^2) is plotted for several values of $N_P = N_{P(1)} + N_{P(2)}$ and N_{Br} where N_j is the number of scattering atoms j at a distance R_j to the absorbing atom. In this fit, which minimized at $N_P = 3$ and $N_{Br} = 1$, only integral $N_{P(1)}$, $N_{P(3)}$, and N_{Br} values were used.

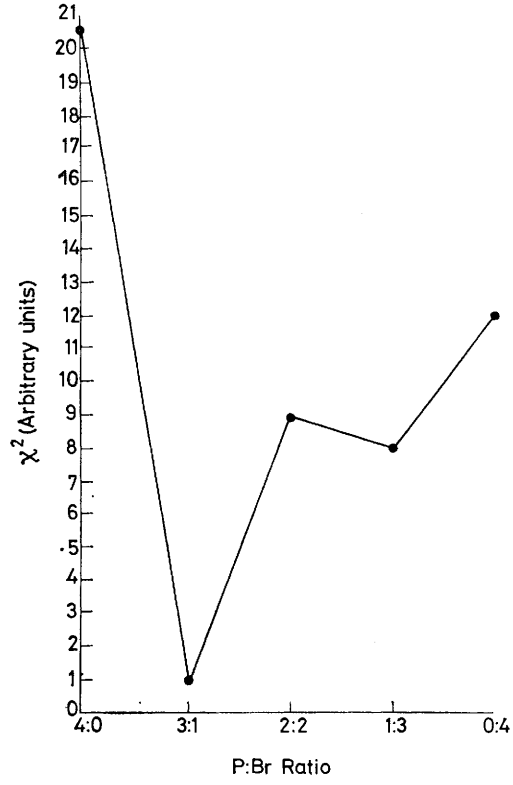

FIGURE 3. Plot of χ^2 (sum of squares of residuals) *vs.* P:Br ratio. χ^2 minimum occurs at a P:Br ratio of 3:1.

TABLE 2. Comparison of distances in $[RhBr(PPh_3)_3]$ and $RhCl(PPh_3)_3$]

	$[RhCl(PPh_3)_3]$		$[RhBr(PPh_3)_3]$	$[RhBrP(C_6H_4CH(CH_2\text{-}o)_3]$
	X-Ray[a]	EXAFS	EXAFS	*X*-Ray[b]
Rh–X	2·37	[1][c] 2·35(1)	[1][c] 2·54(1)	[1][c] 2·587(3)
Rh–P(1)	2·214	[1] 2·23(1)	[1] 2·18(1)	[1] 2·176(10)
Rh–P(2)	2·33	[2] 2·35(1)	[2] 2·31(1)	

[a] From refs. 5 and 6. [b] From ref. 7. [c] Number of bonds of this type.

In the similar chlorotris(triphenylphosphine)rhodium(I) complex,[12] the distances which were determined by the Rh-EXAFS yielded results which were in agreement with

those determined by *X*-ray crystallography[5,6] (see Table 2). In $[RhBr(PPh_3)_3]$ as in $[RhCl(PPh_3)_3]$, two of the Rh–P distances are longer than the third. This suggests that there must be an electronic effect, causing the *trans* influence of P to be greater than that of Br. The geometry of the co-ordination polyhedron about the rhodium atom in $[RhBr(PPh_3)_3]$ was not determined by the EXAFS technique. However, in view of the d^8 electronic configuration, and the *X*-ray structure of $[RhCl(PPh_3)_3]$, $[RhBr(PPh_3)_3]$ is considered to be approximately square planar.

This technique and results reported herein demonstrate the practical application of EXAFS to the solution of structure problems, as a supplement to *X*-ray crystallography.

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