hence[39] $k_c \approx 1.5 \times 10^8$ s^{-1} at this temperature. For the reaction[38]

$$Ph\!-\!\overset{\triangle}{\underset{Ph}{\diagdown}}\cdot \quad \xrightarrow{k_R} \quad Ph_2C\dot{=}CH\dot{=}CH_2$$
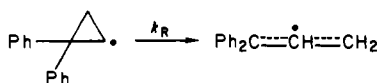
we estimate that $k_R/k_H{}^{Sn} \approx 0.03$ M at 78 °C, hence[39] $k_R \approx 4 \times 10^6$ s^{-1} at this temperature.

We are confident that the kinetic data summarized in Tables I and II will find wide and general use in mechanistic and synthetic studies.

Experimental Section. Tri-*n*-butylstannane was purchased from Aldrich and used as received. Tri-*n*-butylgermane was prepared by reduction of tri-*n*-butylgermanium chloride by lithium aluminum hydride.[40,41] Benzoyl peroxide was obtained from Aldrich and purified by standard methods. Bis(cyclopropylformyl) peroxide[42] and 3,3-dimethylacryloyl peroxide[43] were prepared by literature methods.

Laser Flash Photolysis Experiments. Samples (2 mL, 0.2 M peroxide) were contained in 7 × 7 mm^2 cells made of Suprasil and were deoxygenated by purging with oxygen-free nitrogen. A Lumonics TE-860-2 excimer laser (Xe–HCl–He mixture) with pulses at 308 nm (~4 ns, up to 80 mJ/pulse) was used for sample excitation. Further details on the laser flash apparatus have been given elsewhere.[44]

Registry No. *n*-Bu$_3$Sn·, 688-73-3; *n*-Bu$_3$Ge·, 998-39-0; C$_6$H$_5$·, 2396-01-2; (CH$_3$)$_2$C=CH·, 33825-33-1; *c*-C$_3$H$_5$·, 2417-82-5; (CH$_3$)$_3$CCH$_2$·, 3744-21-6.

Supplementary Material Available: Tables III–IX giving detailed kinetic data (11 pages). Ordering information is given on any current masthead page.

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Nature of the Cadmium Sites in Rat Liver Metallothionein 1 from Cd K-Edge EXAFS

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The Metallothioneins are a unique and widely distributed group of metal binding proteins. They are characterized by their low molecular weight (ca. 6000), high cysteinyl content, and ability to bind substantial numbers of a wide variety of metal ions. The majority of mammalian metallothioneins may be separated by ion-exchange chromatography into two main isoforms, designated as metallothioneins 1 and 2, which differ in their overall negative charge and details of their amino acid composition. However, the number and position of the cysteinyl residues in the polypeptide chain is highly conserved with the sequence -Cys-A-Cys- being predominant.[1] Although crystals of metallothionein have been

isolated, an X-ray crystal structure of the protein has not yet been reported and the information concerning the nature of the metal sites has been obtained from various spectroscopic studies.[2] The general consensus is that the metal atoms are bound by the cysteinyl sulfurs and this has been confirmed for Zn(II)[3] and Cu(I)[4] from K-edge EXAFS data. [113]Cd NMR spectroscopy has been very informative concerning the nature of Cd-metallo-thioneins.[5–9] The occurrence of the resonances at 600–700 ppm downfield of Cd(ClO$_4$)$_2$ has generally been taken as indicative of Cd(Scys)$_4$ coordination. Data for [113]Cd-enriched samples not only clearly indicate different Cd sites but also demonstrate the existence of close Cd···Cd approaches. Furthermore, the information obtained from [113]Cd-decoupling experiments led Otvos and Armitage to propose[8] that Cd$_7$-metallothionein contains two distinct metal aggregates, involving four and three metal atoms in which each metal is tetrahedrally coordinated by four cysteinyl sulfurs; all 20 cysteinyl residues are involved as terminal or μ_2 ligands. These [113]Cd NMR studies have been very influential in respect of the considerations of the binding of other metals by metallothioneins.

Therefore, we considered that it was important to provide alternative structural information concerning the environment of Cd in metallothionein. The availability of a significant X-ray flux at the wavelength of the cadmium K-edge ($\mu = 0.46$ Å) from the Wiggler magnet of the synchrotron radiation source (SRS) at the Daresbury Laboratory has enabled the X-ray absorption spectrum of cadmium in rat liver metallothionein 1 to be recorded. This is the first time the nature of a cadmium site in a biological system has been probed by X-ray absorption spectroscopy and the results obtained are complementary to the [113]Cd NMR data obtained for this protein.[5–9]

Rat liver Cd/Zn-metallothionein 1 was isolated from rats injected intraperitoneally when an aqueous solution of CdSO$_4$ (0.5 mg of Cd per kg of body weight on day one, followed by five injections of 2.0 mg of Cd per kg of body weight on alternate days). Metallothionein 1 was purified,[10] by a combination of gel filtration and ion exchange chromatography, and freeze-dried. The product was electrophoretically homogeneous and contained 7 mol of metal/mole of protein with a Cd:Zn ratio of 1.3:1. Fully substituted Cd$_7$-metallothionein was prepared by treating an aqueous solution of the Cd/Zn-metallothionein-1 with a 10-fold molar excess of CdSO$_4$. After incubation for 12 h at 1 °C, the protein was separated from Cd^{2+} and Zn^{2+} by gel filtration on Sephadex G.25, using distilled water as eluant, and then freeze-dried. The product contained no Zn.

Samples of freeze-dried rat liver Cd/Zn-metallothionein 1, Cd-metallothionein 1, and finely ground CdS diluted with boron nitride were mounted in sample cells of an aluminum sheet 1-mm thick and 1.5 × 2 cm in cross-section, in which a window 3 × 15 mm had been cut; each sample was contained between Sellotape windows. The cell was mounted in an evacuated cryostat and the sample cooled to ca. 77 K. X-ray absorption spectra in the transmission mode were obtained on the EXAFS station of the beam-line of the 4.5 T Wiggler magnet at the SRS. During the experiments, the SRS was operating at an energy of 1.8 GeV with an average current of 180 mA. A channel-cut Si 220 crystal

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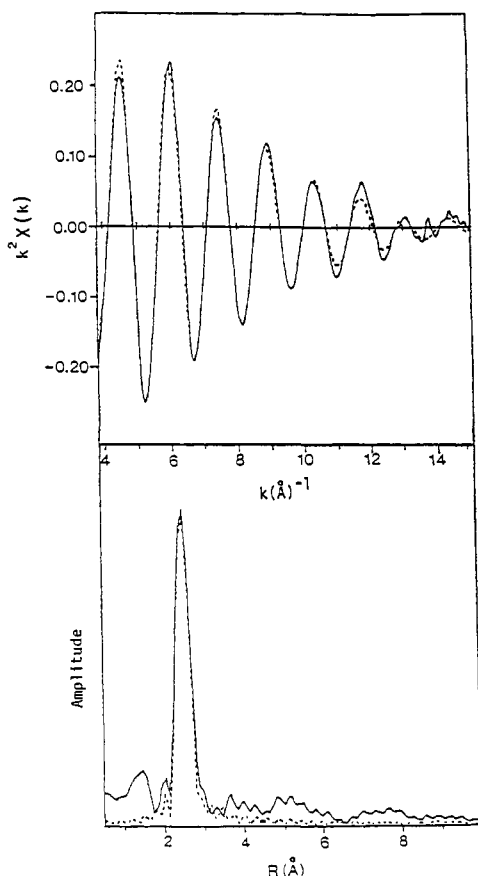
Figure 1. (—) EXAFS (xk^2) associated with the Cd K-edge of Rat Liver Cd/Zn-metallothionein 1 and its Fourier transform. (---) Simulated data for four Cd–S distances of 2.53 Å with a Debye–Waller parameter of 0.013 Å^2.

monochromator was used and data were recorded from 300 eV before the cadmium K-absorption edge up to 1500 eV beyond the edge. Several (ca. four) scans were recorded for each sample and the data were averaged. No signs of radiation-induced damaged were observed (i.e., the spectrum did not change upon exposure to the X-rays). Data analysis, utilizing the single-scattering spherical-wave method for calculating the EXAFS with phase-shifts derived from ab initio calculations,[11–13] the determination of the quality of fit, and the refinement were accomplished as described previously.[14]

No significant difference was detected between the EXAFS associated with the cadmium K-edge of Cd/Zn-metallothionein 1 and that for Cd-metallothionein 1. The EXAFS (×k^2) associated with the cadmium K-edge of Cd/Zn-metallothionein 1, a successful simulation, and the corresponding Fourier transforms are shown in Figure 1. The cadmium K-edge EXAFS of Cd/Zn- and Cd-metallothionein 1 are consistent with each cadmium atom having an environment consisting of a single shell of four sulfur atoms at 2.53 (2) Å. No indication of any Cd⋯Cd back-scattering was manifest in the EXAFS and the introduction of oxygen or nitrogen back-scattering contributions at chemically reasonable distances significantly deteriorated the quality of the agreement between the stimulated and the experimental data. The reliability of the EXAFS interpretation receives justification from the 2.52 (1) Å obtained for the Cd–S distance in CdS, as compared with the crystallographic value of 2.52 Å.[15] The Cd–S distance and

coordination number obtained for cadmium in metallothionein 1 are not unexpected, given the known thiolate chemistry of this element.[16]

The structural information presented herein strengthens the interpretation of the [113]Cd NMR data obtained for metallothioneins[5–9] and is compatible with the proposals of Otvos and Armitage.[8] The EXAFS results demonstrate that the chemical inequivalence observed by [113]Cd NMR does not arise from marked variations in atom type, coordination number, or metal–ligand distances within the metals' first coordination sphere. Small differences (ca. 0.02 Å) between Cd–S distances, perhaps due to the presence of bridging and terminal thiolato groups, would be consistent with the EXAFS data.

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Ligand-Induced Reactions of a Directly Bonded Early–Late Transition-Metal Complex Involving Reversible Cleavage of a Zr–Ru Bond with Expulsion of a Ruthenium Hydride

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Heterobimetallic complexes in which an early transition metal is directly bonded to a late transition metal are interesting as potential precursors of new types of hydrogenation catalysts. Recently we reported the synthesis of a series of metal–metal-bonded zirconium–iron and zirconium–ruthenium complexes[1] and of the novel zirconium–diruthenium complex $(C_5H_5)_2Zr[Ru(C-O)_2(C_5H_5)]_2$ (**1**).[2] Here we report the unprecedented reactions of **1** with added ligands that lead to expulsion of $(C_5H_5)Ru(CO)_2H$ and formation of C_5H_4Zr products or intermediates.

When a dark-orange C_6D_6 solution of **1** under 700 mm of CO was monitored by ^{1}H NMR, the slow ($t_{1/2} \sim 3$ h) formation of $(C_5H_5)Ru(CO)_2H$ and a new heterobimetallic complex **2** containing two equivalent Cp's on Zr (δ 5.10) and a mirror-symmetric C_5H_4 ligand (δ 4.78, 3.93) was observed and the solution became light orange. When a slurry of **1** (140 mg) in 1:1 toluene/ether was stirred under CO for 48 h, **2** (70 mg, 70%) precipitated from solution as a yellow powder.

The structure of **2** was determined by X-ray crystallography[3] (Figure 1). The Zr and Ru centers of **2** are linked both by a metal–metal bond and by a bond from Zr to the η^5-C_5H_4 ligand on Ru. This Zr–C bond is bent 34° below the plane of the C_5H_4 ligand.[4] The zirconium-bound CO is bent slightly away from Ru (Zr–C–O 167°) indicating a very weak interaction with the remote (2.70 Å) Ru.

When a C_6D_6 solution of **1** was treated with PMe$_3$, the formation of $(C_5H_5)Ru(CO)_2H$ and a new heterobimetallic com-

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