Kinetic and Structural Information on Metal Cluster Rearrangement in Solution from EXAFS Spectra

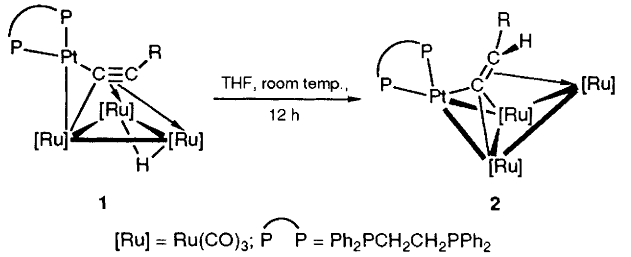
Andrew J. Dent,[a] **Louis J. Farrugia,**[b] **A. Guy Orpen**[c] **and Susan E. Stratford**[c]

[a] *SERC Daresbury Laboratory, Warrington WA4 4AD, UK*
[b] *Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK*
[c] *School of Chemistry, University of Bristol, Bristol BS8 1TS, UK*

Pt L_{III} edge EXAFS spectra for the spiked triangular cluster $[Ru_3Pt(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-CCBu}^t)(CO)_9(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane] **1** measured during its rearrangement in solution into the butterfly cluster $[Ru_3Pt(\mu_4\text{-}\eta^2\text{-C=CHBu}^t)(CO)_9(dppe)]$ **2** show substantial changes, which provide both structural data on the complexes in solution and kinetic information on the course of the reaction.

Formation of metal–metal bonds is fundamental to the construction of molecular metal cluster complexes and by implication to the aggregation of metal atoms required to form metal crystallites in heterogeneous systems such as bimetallic catalysts.[1] While reactions in which metal–metal bonds are formed are well known,[2] especially in solution, techniques for following these fundamental processes *in situ* are scarce. To date, the bulk of information on cluster assembly has been provided by the isolation and structural characterization (by crystallography) of thermodynamically stable intermediates. Some spectroscopic studies on metal cluster assembly have been reported,[3] but an important drawback of NMR (and other spectrosopic techniques) is that they can at best only provide information about the metal-core *symmetry*, usually in an indirect fashion. By contrast, EXAFS spectroscopy is able to provide *direct* structural information in solution on metal–metal distances and coordination numbers, and hence on cluster core geometry. In this paper we show that it is possible to follow the geometric changes during rearrangement of the metal skeleton of clusters in solution using EXAFS spectroscopy.

Heteronuclear clusters containing platinum[4] show a structural flexibility associated with varying 16- or 18-electron count at the platinum atoms. In recent studies we have shown[5–7] that differing core geometries are readily adopted by triruthenium–platinum clusters. In particular, solution NMR studies show that the *spiked triangular* cluster $[Ru_3Pt(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-CCBu}^t)(CO)_9(dppe)]$ **1** [dppe = 1,2-bis(diphenylphosphino)ethane] rearranges at room temperature in tetrahydrofuran (THF) into the vinylidene cluster $[Ru_3Pt(\mu_4\text{-}\eta^2\text{-C=CHBu}^t)(CO)_9(dppe)]$ **2** (see Scheme 1), which has a *butterfly* Ru_3Pt core.[5] This reversible, intramolecular rearrangement shows an inverse kinetic deuterium isotope effect ($k_H/k_D = 0.56$) and follows first-order kinetics ($k = 3.3 \times 10^{-3}$ min^{-1} at 302.5 K).[6] Equilibrium is reached after *ca.* 12 h and lies in favour of cluster **2** ($K_{eq} = 9$).



Scheme 1

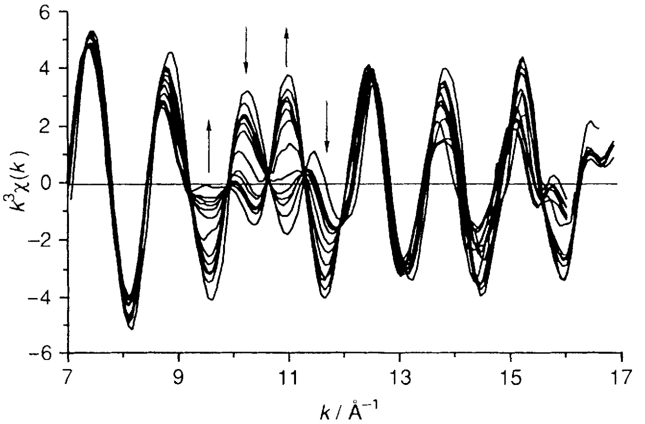


Fig. 1 Observed k^3-weighted Pt L_{III}-edge EXAFS spectra in the range k = 7–17 Å^{-1} for the rearrangement of **1** into **2** in 80 mmol dm^{-3} THF solution. Measurements were made at intervals (see Fig. 2) over a 12 h period. Arrows indicate the direction in which features develop over the period of measurement.

Platinum L_{III}-edge EXAFS spectra for pure samples of **1** and **2** in the solid state yield structural data (number and distances of Pt–Ru, Pt–P distances *etc.*) by conventional model fitting procedures,† which were in excellent agreement with their known[5] crystal structures. In addition, analysis of EXAFS data for their solutions in THF, both frozen and at ambient temperature, showed their solution-phase structures to be essentially identical to those in the solids. This observation and the significant differences between the EXAFS of **1** and **2**, gave us hope that EXAFS spectra measured *in situ* for the interconversion of **1** and **2** would yield information on the progress of the rearrangement.

In fact Pt L_{III}-edge EXAFS spectra measured on a THF solution of cluster **1** at ambient temperature show substantial

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† Compounds **1** and **2** were prepared and isolated by literature methods[5] and used for EXAFS measurements on pure samples as solids and in frozen THF solutions. For measurements in solution on the rearrangement of **1** into **2**, THF was added to a freshly prepared sample of **1** and successive EXAFS spectra were measured over a period of *ca.* 12 h at ambient temperature in a sealed and unstirred cell. Each spectrum was acquired over a *ca.* 20 min period with 11 spectra in all being obtained. The spectra for pure **1** and pure **2** in frozen THF solution have been included in Fig. 1 in addition to the *in situ* spectra. Platinum L_{III} absorption edge EXAFS data were collected at the Daresbury SRS on station 7.1 in transmission mode. Solid samples were typically of *ca.* 1 mm thickness and were diluted in boron nitride in order to achieve changes in $\log(I_0/I)$ in the range 1–2 at the absorption edge. Solution samples were measured in cells of thicknesses between *ca.* 3 mm in order to achieve changes in $\log(I_0/I)$ in the range 1–2 at the absorption edge. Raw data were corrected for dark currents and converted into k-space (with EXCALIB[8]), and backgrounds subtracted (with EXBACK[8]) to yield EXAFS functions $\chi^{obs}{}_i(E - E_0)$. These were Fourier filtered (window from 1.2 to 25 Å) to remove features at distances below *ca.* 1.2 Å but not to remove long distance features of the quasi-radial distribution function (*i.e.* no noise removal was attempted). Model fitting was carried out with EXCURV90,[8] using curved-wave theory. Only shells significant at the 99% level[9] were included in final models. Full details of the final models employed are available from the authors on request. *Ab initio* phase shifts and back-scattering factors using spherical-wave theory with 25 l values were used throughout. Phase shifts, and the values used for the proportion of absorption leading to EXAFS (AFAC = 0.8) and the magnitude of inelastic effects modelled by an imaginary potential (VPI = −4.0 eV), were assigned on the basis of fits to data for the compounds **1** and **2** in the solid state.

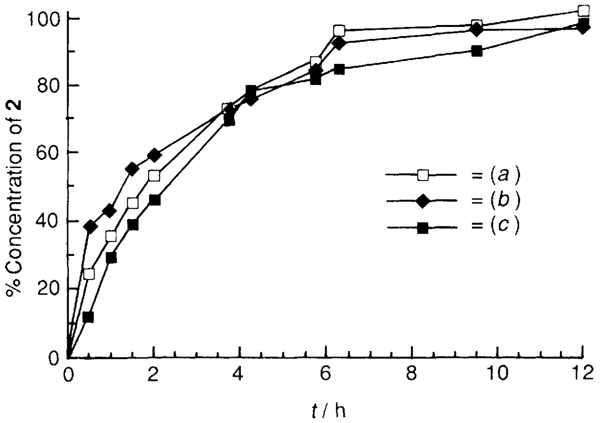

Fig. 2 Concentration of **2** as a function of time as estimated by linear combinations of t = 0 and t = 12 h spectra to fit the variation of the EXAFS function at (*a*) k = 9.7; (*b*) k = 10.5; (*c*) k = 11.2 Å^{-1}.

and monotonic changes over a 12 h period as **1** rearranges into **2** (see Fig. 1). Particularly notable is the series of clearly defined isosbestic points in the region from k = 9–12 Å^{-1} of a type familiar from UV–VIS spectroscopic kinetic studies. Similar isosbestic points are clearly observable in the sine transforms of these spectra. Linear combination of the first and last spectra provide good quality fits of the observed intermediate spectra thereby allowing estimation of concentration variation as a function of time from the coefficients used (see Fig. 2). In turn this provides the information required to calculate a rate constant for the reaction, the value of which (*ca.* 6 × 10^{-3} min^{-1}) is comparable‡ with that derived from NMR data. Furthermore, these results show that no intermediate species are formed in detectable concentrations during the reaction.

In principle the presence of two metallic elements in **1** and **2** should allow the extraction of enhanced structural information by use of both Ru K-edge and Pt L_{III} EXAFS data, a point we will develop in a full report of this work. In practice the Pt L_{III} EXAFS is much more sensitive to the change in cluster geometry (from **1** to **2**) because the number of ruthenium atoms in the first 'coordination shell' of platinum increases by one (from 1 to 2), while the *average* number of platinum atoms in the ruthenium coordination sphere by only one third (from 0.33 to 0.67). Therefore, in this system the platinum is the more effective reporter element for EXAFS study.

In conclusion, we believe that this work provides evidence that it will be possible to obtain both structural and kinetic imaging of the reaction profile for a variety of solution-phase reactions from EXAFS data. Given the current efforts to develop energy dispersive and quick EXAFS techniques capable of giving useful data on much reduced timescales the way is open for application of this approach to a wide range of solution and solid-state chemistry.

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‡ EXAFS spectra on the reaction mixture were measured at ambient temperature, measured as 24.5 °C.