Plenary and Session Lectures

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New Stoichiometric and Catalytic Organometallic Chemistry with Actidines. C–H Activation and Phosphine/Phosphite Coordination Chemistry

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Some Stereochemical Aspects of Actinide Coordination Chemistry

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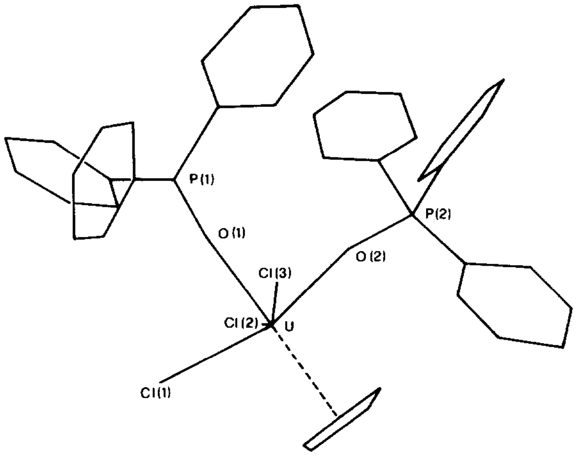
It has been recognised for many years that ligand field interactions are at best minimal in 5f transition element chemistry, and that such interactions will contribute very little to the kinetic stability of the complexes formed by these elements. Consequently such complexes can be regarded as kinetically labile, and there will be a considerable degree of flexibility in the coordination geometries adopted by the complexes formed with these elements. In addition, ligand exchange reactions occur quite readily, simply because there is little or no gain (or loss) of ligand field stabilisation energy involved in an intra- or intermolecular rearrangement. In such systems the steric crowding about the central metal atom becomes the most important factor in determining the coordination number and geometry adopted in both lanthanide and actinide complexes, which has led to many publications in recent years aimed at investigating the effects of bulky ligands on the stoichiometries of the complexes formed by these elements [*e.g.* 1–3]. Until recently, no attempts have been made to quantify the effects of steric crowding in actinide complex systems. The first systematic approach to this type of problem was made by Tolman [4], who used a 'cone-angle approach' to describe the size of phosphorus ligands, and this idea was extended by others [5, 6] who also introduced the idea of ligand profile. However, these approaches to the problem were more two-dimensional in character than three-dimensional, and in order to achieve some understanding of general steric effects which are neither restricted to a special type of ligand, nor restricted to systems in which one part of the coordination environment is left unchanged while the other parts are varied, one needs to go beyond the Tolman approach in order to obtain a unique description of steric crowding. Dr. Li Xing-fu in my group has done this by looking at the problem in terms of the actual solid angles subtended by the ligands in a given complex to the centre of the metal atom concerned [7, 8].

In order to apply this treatment one must distinguish between the first order steric crowding due to the atoms or groups of atoms directly bonded to the metal atom and the second order crowding which arises from the other atoms or groups of atoms bonded to the donor or other atom involved in bonding to the metal. To make this clear, consider the structure of the complex $[(\eta^5\text{-}C_5H_5)UCl_3(PPh_3O)_2]$ [9] shown below.



In this structure, two PPh_3O molecules occupy *cis* positions in a pseudooctahedral geometry. The first order crowding is caused by the C_5H_5 group, two oxygen atoms from the PPh_3O molecules and three chlorine atoms, while the second order crowding arises from the six C_6H_5 groups of the two PPh_3O molecules. The distances between the chlorine atoms and hydrogen atoms of the PPh_3O ligands are much greater than the sum of the Van der Waals' radii, so their interactions are negligible, and by meshing the C_6H_5 rings into the gaps between adjacent molecules of the Ph_3PO ligands, repulsions between the C_6H_5 groups from the two Ph_3PO molecules can be avoided. If these rings do not mesh in this way,