New Large Molecules Contain Ruthenium

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Of all the platinum group metals, rhodium is, perhaps, the most notable. It is the most expensive, costing about $2000 per ounce in 1992, though today it is typically around $700 per ounce. This price is largely a result of its scarcity, but also because of its important catalytic applications. Rhodium is an excellent catalyst for so many processes, from the Monsanto acetic acid synthesis to the selective hydrogenation of alkenes, and in such reactions rhodium is superior to most other catalysts.

By comparison, ruthenium, which is one of

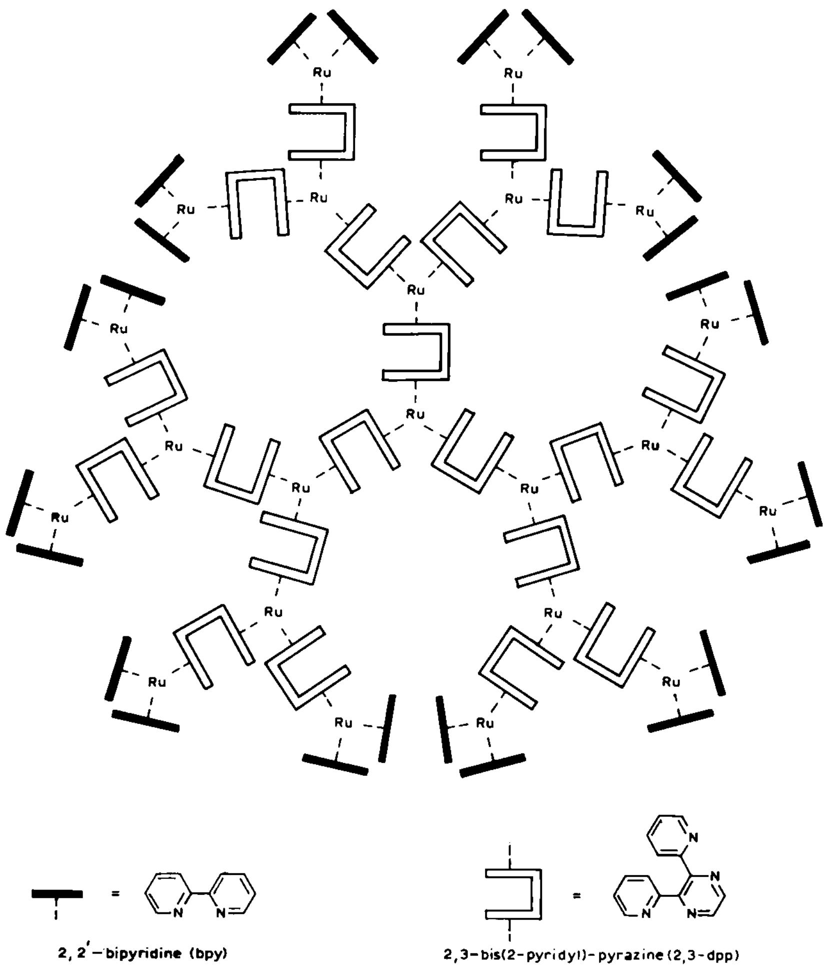

Fig. 1 A dendritic co-ordination complex held together by 22 ruthenium atoms. (Structure adapted from Ref. (2))

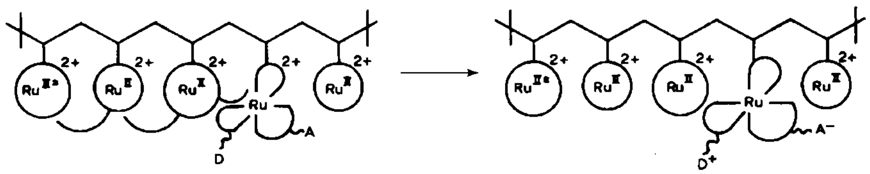

Fig. 2 A reaction of a polymer-supported ruthenium complex induced by light (Ref. 3)

its nearest neighbours in the Periodic Table, is a much cheaper metal, costing around $27 per ounce today, and in the past this metal has been overlooked. Ruthenium does, however, have good catalytic properties, for instance for the hydrogenation of carbon monoxide in the Fischer-Tropsch reaction, although iron is the metal that is commonly utilised for this reaction. Iron performs well catalytically and is very much cheaper than ruthenium; it is therefore used in preference to ruthenium in commercial plants, such as the giant SASOL plants in South

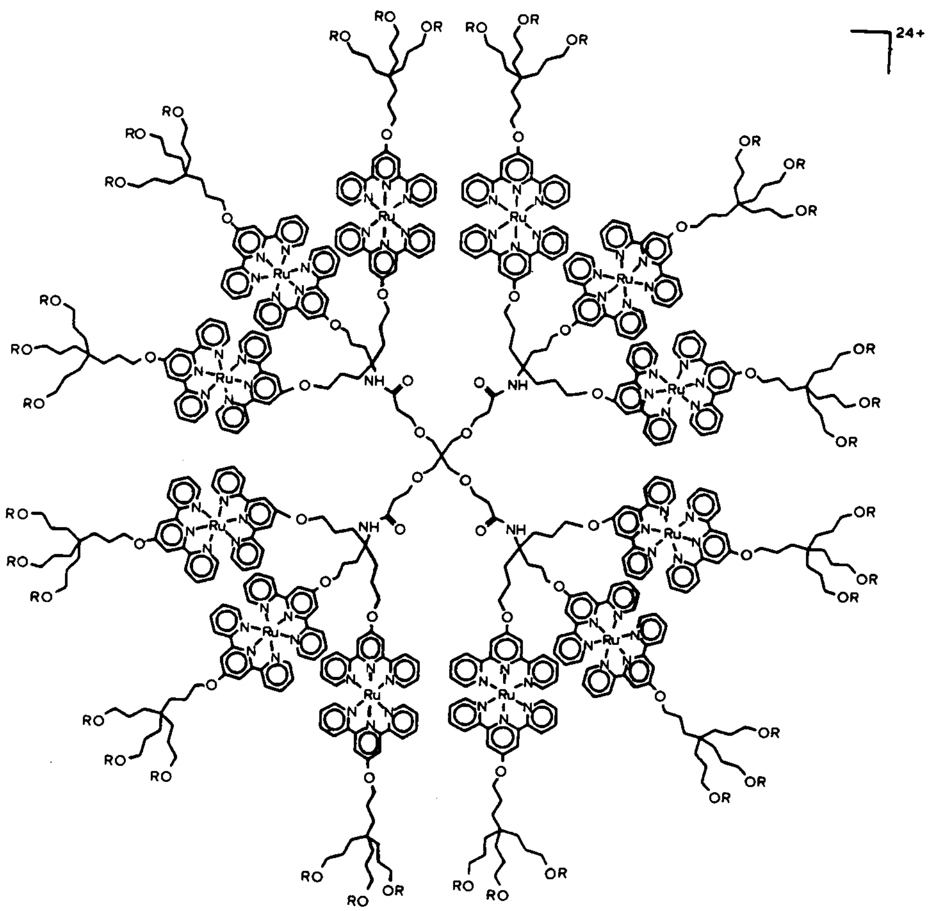

Fig. 3 A new type of dendritic co-ordination complex containing 12 ruthenium atoms (Ref. 5)

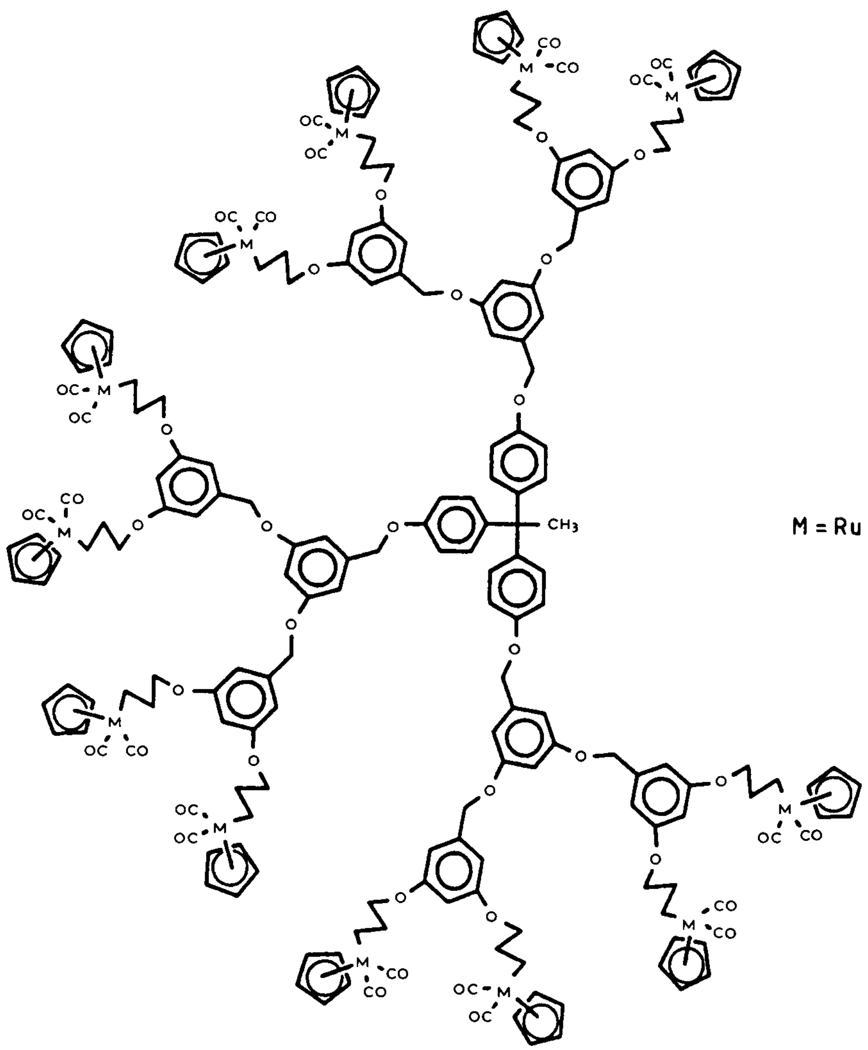

Fig. 4 An organometallic dendrimer containing 12 ruthenium atoms obtained by reacting a second generation dendritic wedge with a trifunctional core (Ref. 6)

Africa. Nevertheless, ruthenium is thought by many to be a better catalyst than iron for the process.

Rhodium is a good catalyst, partly because it forms labile complexes. Compared with rhodium, ruthenium often forms more stable metal-ligand bonds, which is not good for catalytic reactions but is essential for building up large molecules, where it is important to have thermodynamically strong bonds and kinetically inert complexes. Indeed, ruthenium is particularly well-suited to this task, the ruthenium-ligand environment having the capacity to withstand the conditions necessary to build up big molecules.

Thus, it may not be too surprising to learn that four independent research groups in Italy, England, the U.S.A. and South Africa, have recently prepared some of the largest metal complexes known and that all of these very large metal complexes contain ruthenium. For this and other reasons, ruthenium is now becoming much more important.

In 1992 a group in Bologna, Italy, reported an elegant synthesis of a novel dendrimer that is held together by 22 ruthenium atoms and is believed to be the largest co-ordination complex ever made, Figure 1, (1). This complex may well have novel properties and applications, for instance for use in new light harvesting devices for solar energy conversion (1, 2).

At the University of North Carolina the search for artificial photosynthetic reagents is one of the main driving forces of a research group at Chapel Hill, who have recently prepared polymer supported ruthenium complexes (3). These materials are not unimolecular but they are believed to contain about 30 ruthenium atoms co-ordinated through functionalised bipyridyl ligands to a polymer backbone, see Figure 2.

One of the founders of dendrimer research is George R. Newkome, of the University of South Florida, who has synthesised many organic dendrimers by the divergent approach (4). Dendrimers are highly branched polymers and can be considered to be molecular fractals. Collaboration between the group run by Newkome in the U.S.A. with a co-ordination chemistry group headed by E. C. Constable which was based at Cambridge University, U.K., has resulted in the development of a new type of dendritic co-ordination complex containing 12 ruthenium atoms, see Figure 3, (5). More recently, at the University of Cape Town, we have used a convergent approach to prepare the first organotransition metal dendrimers containing ruthenium-carbon σ-bonds (6). Here, the synthesis of discrete molecules each containing up to 12 ruthenium atoms, see Figure 4, was performed in a stepwise process, with the metal atoms being bonded exclusively to the surface of the growing macromolecules. This approach has now been taken further and we have built bigger organometallic dendrimers, up to the 3rd and 4th generations (7).

Attaching a 4th generation dendritic wedge to a trifunctional core has now resulted in a molecule with 48 ruthenium atoms – all in the same molecule, and all being close to the surface of the molecule. While this is probably the largest organometallic complex ever prepared, having a molecular mass of 18,438, it is readily soluble in organic solvents and can be fully characterised by various spectroscopic techniques including NMR and infrared spectroscopy.

Future Applications

The solubility of these organoruthenium dendrimers may be the key to possible applications, since large metal cluster compounds are often insoluble. Thus, for example, these organometallic dendrimers may find use in the preparation of thin metallic films. In the unique molecular architecture of the ruthenium dendrimer the ruthenium atoms all lie close to the molecular surface, and this has resulted in a new type of polymer-supported complex which might find application as a novel catalyst, functioning at the interface between homogeneous and heterogeneous catalysts.

Thus, if these recent reports are typical of what can be expected, there will be many more new and exciting complexes which could soon be discovered. The future does indeed look very promising for bigger, and maybe even better, ruthenium complexes.

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