

# Platinum and Palladium Complexes of Unsaturated Hydrocarbons

## A COMPREHENSIVE REVIEW OF THE LITERATURE

To generations of chemists trained before about 1950 the possibility of a marriage between organic and inorganic chemistry was rarely considered. These two sub-divisions of chemistry remained in separate water-tight compartments, and only the unusually inquiring or perspicacious research man dared to explore the boundaries. Within the space of twenty years a complete transformation has occurred: beginning with the discovery of ferrocene, a very large number of compounds are known in which organic molecules or derivatives thereof are combined with inorganic salts to form complexes of great interest and usefulness. The study of these complexes constitutes organometallic chemistry, and with it has come the realisation that the previous sub-divisions were artificial and restrictive, and that the interaction of one on the other is both stimulating and necessary. Our concept of chemical bonding has been greatly extended through the study of organometallic complexes, and the end of our increasing understanding of the fundamentals of chemical forces is not yet in sight.

Of the many types of organometallic complexes, those formed between unsaturated hydrocarbons and palladium and platinum in their  $d^8$  (i.e.,  $Pd^{II}$  and  $Pt^{II}$ ) and  $d^{10}$  (i.e.,  $Pd^0$  and  $Pt^0$ ) states are among the most fascinating and useful. A comprehensive and scholarly review of them by F. R. Hartley of the Commonwealth Scientific and Industrial Research Organisation of Australia, has recently appeared (1), reviewing the literature up to mid-1968 and containing no less than 605 references. It is impossible to do full justice to such a valuable survey in a short review; one can do little more than indicate the ground which is covered.

The bond formed between ethylene and, say, a palladous ion consists of two parts: in one part, referred to as the  $\sigma$ -bond,  $\pi$ -electrons from the olefin are donated to a vacant orbital of the ion, while in the other part, referred to as the  $\pi$ -bond, electrons from an orbital of the ion are back-donated into vacant anti-bonding orbitals of the ethylene. As a result, changes occur in the structure of the ethylene which are detectable in X-ray structure analysis, by infra-red and nuclear magnetic resonance spectroscopy. In complexes of  $Pd^0$  and  $Pt^0$ , however, the  $\pi$ -character of the bond is almost entirely absent, as is also the case with acetylene complexes. In the tetracyanoethylene complex with  $Pt^0$ , and with acetylene complexes, the bonding is almost pure  $\pi$  in character because of the weak donor ability of the hydrocarbon. The strength of the olefin to metal bond is measured as a "stability constant", and numerous values are quoted in this review: complexes with  $Pt^{II}$  are however notably stabler than those with  $Pd^{II}$ . Much stronger complexes are formed by non-conjugated diolefins such as 1,5-cyclooctadiene, but the increased stability is predominantly due to the fact that two olefin-metal bonds are formed.

Particular interest attaches to olefin-metal complexes by reason of their being intermediates in a number of important homogeneously catalysed processes. The action of coordination renders the olefin more susceptible to nucleophilic attack, for example, by hydroxyl and acetate ions, than is the free olefin, and this enables the well-known Wacker reaction (the oxidation of ethylene to acetaldehyde) to occur, and also the oxidation of ethylene to vinyl acetate. Significantly, only

$\text{Pd}^{\text{II}}$  and not  $\text{Pt}^{\text{II}}$  complexes are sufficiently reactive: this results from the lower stability of the former, referred to above. Other potentially important homogeneous processes involving metal-olefin complexes as intermediates are carbonylation, hydrogenation, isomerisation, and polymerisation.

The concept of donor-acceptor bonding in olefin-metal complexes has also been applied to understanding the mechanisms of heterogeneous catalysis (2), as well as in other areas of organometallic chemistry. It forms a basis for rationalising the properties and reactivities of olefin-metal complexes and possibly for

predicting more reactive complexes for homogeneous catalysis.

It is unfortunate, but perhaps inevitable, that Dr Hartley's review was not extended to cover the remaining platinum group metals, for there are interesting trends in the stability of olefin-metal complexes in passing through ruthenium, rhodium and palladium, and also systematic differences between the second and third row metals.

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### References

- 1 F. R. Hartley, *Chem. Rev.*, 1969, **69**, 799
- 2 G. C. Bond, *Platinum Metals Rev.*, 1966, **10**, 87

## Light Duty Electrical Contacts

### THE SELECTION OF MATERIALS

It is not so very many years ago that an electrical contact operating of course in a fairly simple circuit – could be more or less adequately described as either “good” or “bad”. More recently, and in particular during the last fifteen years, the study of electrical contact phenomena has been greatly stimulated by the rapid developments in electronics and in automation and control, so that a much more sophisticated approach has been necessary to the proper understanding and selection of contact materials.

In the light duty field – which may be broadly defined as involving currents of not more than 1.0 A at voltages of the order of 250, down to very small radio and audio-frequency currents – the primary consideration is the use of surfaces free from tarnish films in order to ensure minimum contact resistance. For this basic reason the platinum metals and gold, with a number of their alloys, comprise the materials from which a final selection has to be made to suit individual conditions. A useful and comprehensive survey of this subject has just been published in the series of *Metallurgical Reviews*, sponsored by the Institute of Metals, prepared by H. C. Angus of International Nickel (*Met. Rev.*, 1970, **15**, 13). This covers the production, properties, and behaviour of contact materials with a reasonable minimum of the mathematics involved in modern contact theory. The literature on contact physics has become extensive in recent years – par-

ticularly from the researches of Ragnar Holm and Professor Llewellyn-Jones – and it is valuable to have a full and up-to-date review.

The factors involved in the selection of contact materials are outlined – their density, electrical and thermal conductivities, hardness, melting and boiling points – and these are discussed in relation to the range of gold and the platinum metals and their alloys. While gold has the highest conductivities, it is soft and mechanically weak and has the lowest boiling point (a factor of more importance than might readily be supposed in relation to the very high local temperatures attained at contact surfaces), rhodium, ruthenium, and iridium are difficult to fabricate so that little or no advantage has yet been taken of their high boiling points combined with reasonably good conductivities. Thus platinum and palladium provide the great bulk of light duty contacts, but improved methods of fabricating the more refractory platinum metals should lead to their more extensive use as relay contacts.

A marked feature of contact technology in the last few years has been the great increase in the use of electrodeposited surfaces, particularly with alloyed golds, but improved electrolytic processes for platinum and palladium have extended the scope of these metals as contacts, while more recently methods for ruthenium deposition have enabled greater advantages to be taken of its useful properties.

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