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Luis A. Oro and Carmen Claver

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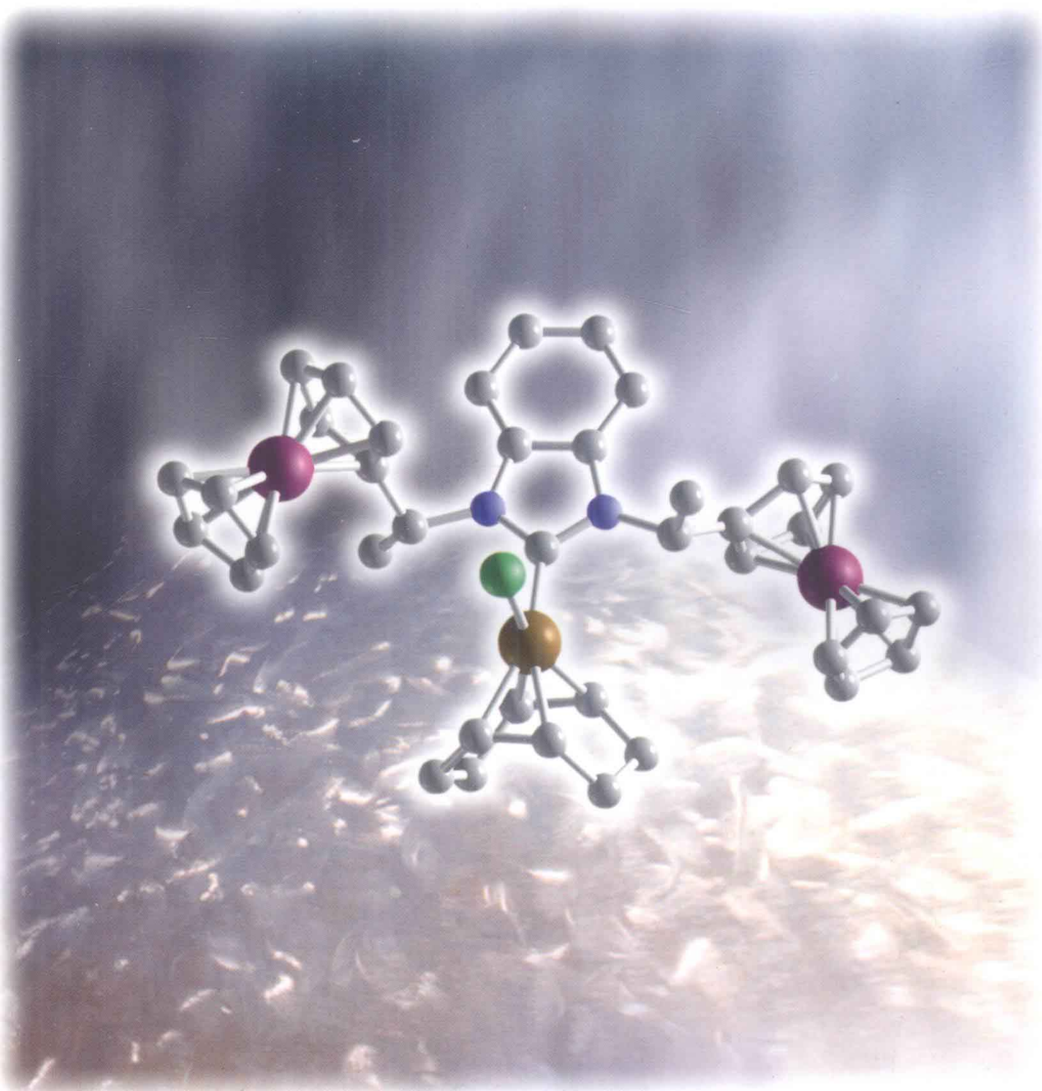
Iridium Complexes in Organic Synthesis



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Further Reading

Hashmi, A. S. K., Toste, D. F. (Eds.)

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Preface

The impressive developments of organometallic chemistry during the past 50 years have allowed the preparation of a wide variety of soluble metal complexes useful for organic transformations under mild conditions. Among these metals, the noble triad of ruthenium, rhodium and palladium has played the major role, with rhodium being the most relevant when acquiring knowledge of the mechanisms of metal-mediated organic transformations. In fact, the discovery and application of Wilkinson's catalyst, $RhCl(PPh_3)_3$, proved to be a major milestone during the mid-1960s, mainly because it led to the initiation of many successful applications, including rhodium-catalyzed olefin hydroformylation, the Monsanto production of acetic acid, and industrial asymmetric hydrogenations. Details of some of the major applications of rhodium complexes were updated in a recent book, *Rhodium-Catalyzed Organic Reactions* (edited by P. A. Edwards, published by Wiley-VCH in 2006). In contrast, iridium complexes have been most often used as model compounds to acquire an understanding of the elementary steps of transition metal-catalyzed reactions. A good example of this was 'Vaska's compound', the details of which were first reported in 1965, and which has since provided valuable information on the oxidative addition reactions that serve as key steps in almost every catalytic cycle. Unfortunately, the $IrCl(PPh_3)_3$ complex – which can be seen as analogous to Wilkinson's catalyst – is not a good hydrogenation catalyst, due mainly to the inability of the $IrH_2Cl(PPh_3)_3$ to lose hydrogen. Nonetheless, a variety of cationic iridium complexes with a phosphine: iridium ratio of 1 to 2 have been used extensively as efficient catalysts for alkene hydrogenation, including the industrial enantioselective hydrogenation of imines. Although iridium complexes are less frequently used than their rhodium analogues, in some processes they may be more effective – the carbonylation of methanol being an excellent example in the arena of bulk chemistry. Perhaps the most important catalytic applications of iridium complexes, however, are in the manufacture of fine chemicals, most notably in areas of chemoselective and enantioselective hydrogenation. Iridium complexes have also been shown to play an important role in the enantioselective hydrogenation of C=N, which is used widely in the fine chemicals industry, and also of non-functionalized C=C bonds, with particular interest being centered on the creation of intermediates and building blocks in organic synthesis.

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Today, although the value of iridium is becoming increasingly recognized in many organic transformations, it is still not used to any great degree by the chemicals industry. So, it is the aim of this book not only to evaluate the potential of the most promising reactions that involve iridium complexes, but also to provide an account of the role of these materials in important organic transformations such as hydrogenation, hydroamination, hydroboration, C—C bond formation, carbonylation and cycloadditions. The use of relevant ligands as carbenes or pincer ligands, as well as recent catalytic systems using iridium nanoparticles, are also described.

We, the editors, believe that organoiridium chemistry has not only a rich past, but that the application of iridium complexes in organic transformations also has a brilliant future!

October, 2008

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