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Preface

Vinylidene, allenylidene, and metallacumulene complexes

The serendipitous discovery of ferrocene in 1951 provided a major impetus to the rapid development of transition metal organometallic chemistry. This development initially emphasized transition metal π-complexes of unsaturated hydrocarbons but also led to new types of transition metal alkyls and aryls containing metal–carbon single σ-bonds. The scope of transition metal organometallic chemistry expanded still further in 1964 when Fischer and Maasbol reported the first transition metal complex of a terminal carbene ligand. Such complexes provided the first unambiguous examples of compounds with a direct transition metal–carbon double bond.

The articles in this special issue of *Coordination Chemistry Reviews* discuss special types of transition metal carbene complexes, namely complexes in which a carbon-carbon double bond is immediately adjacent to the metal-carbon double bond. The simplest such ligands are vinylidene ligands of the general type $[M]{=}C{=}CR_2$, which may be regarded as analogues of allenes in which one of the “end” carbon atoms of the allene chain is replaced by a transition metal unit. The first examples of such vinylidene complexes contained 2,2-dicyanovinylidene ligands of the general type $[M]{=}C{=}C(CN)_2$, originally reported by King and Saran in 1972. Several years later transition metal vinylidene complexes with hydrogen, alkyl, and/or aryl groups rather than the rather special cyano groups began to be reported by a number of research groups and this area of organometallic chemistry has expanded drastically during the past three decades. Ligands found in such complexes include not only vinylidene ligands but also allenylidene ($[M]{=}C{=}C{=}CR_2$) and longer metallacumulene ligands.

Originally these metal vinylidene, allenylidene, and longer cumulene complexes remained largely laboratory curiosities. However, in recent years Grubbs and coworkers have developed some effective and robust olefin metathesis and polymerization catalysts based on ruthenium vinylidene complexes that have generated considerable interest in these previously obscure molecules. Because of this exciting potential application of metal vinylidene complexes, such organometallic compounds have recently generated considerable interest among the community of organometallic chemists. This was reflected, for example, in the relatively large number of papers on vinylidene, allenylidene, and metallacumulene complexes presented at the most recent international conference on organometallic chemistry, which was held in July 2002, in Corfu, Greece.

This special issue of *Coordination Chemistry Reviews* presents ten articles discussing various aspects of the chemistry of vinylidene, allenylidene, and metallacumulene complexes ranging from the original discovery of 2,2-dicyanovinylidene metal complexes to modern applications of vinylidene and allenylidene metal complexes in catalysis. These articles focus particularly on special aspects of the coordination chemistry of transition metals bearing these unusual types of unsaturated carbon ligands. We hope that the readers of these articles will gain insight regarding recent developments in this unusual area of coordination/organometallic chemistry as well as some ideas for new research programs in both pure and applied chemistry.

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