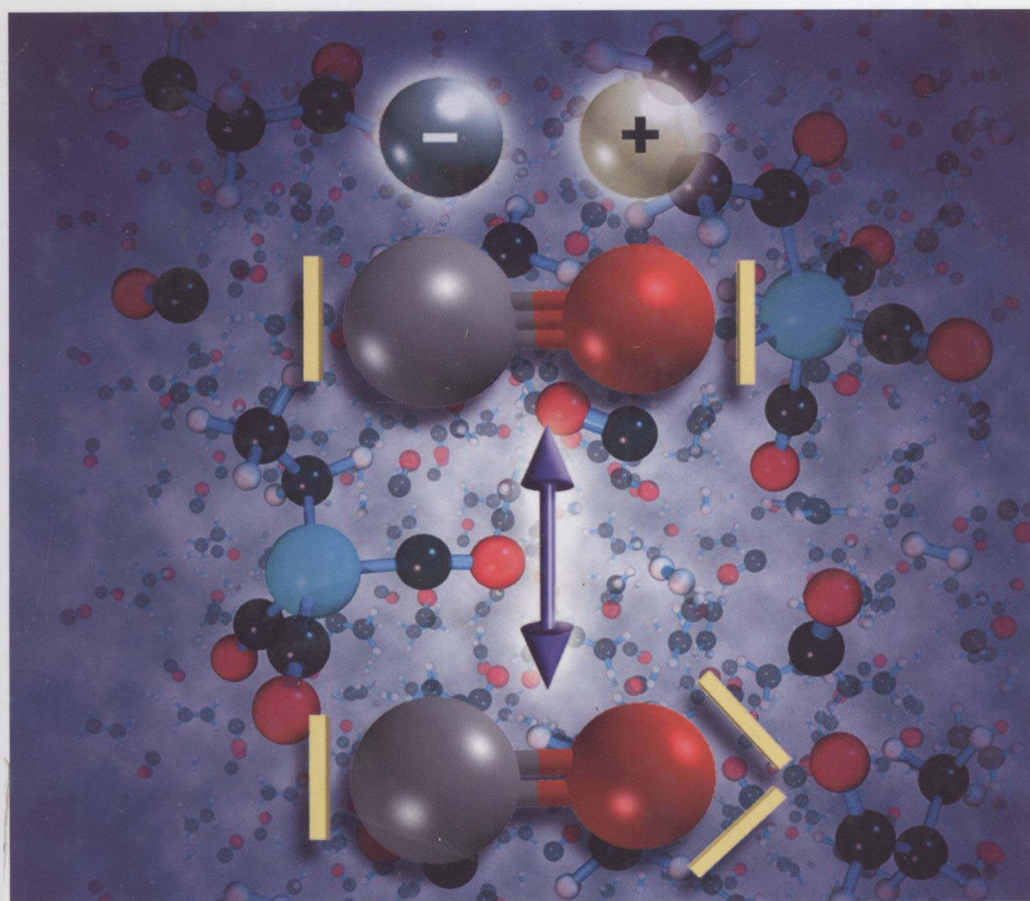


Edited by László Kollár

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# Modern Carbonylation Methods



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*László Kollár*



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## Preface

The organotransition metal chemistry, after an unbelievable expansion in the last decades, reached the stage of general application in synthetic organic chemistry. The recognition of the carbon–metal bonding properties and the mechanistic understanding of the basic catalytic reactions, as well as the definition of the scope and limitations, have rendered many of the transition metal-catalyzed reactions, among them carbonylation reactions involving the use of carbon monoxide as reactant, the most efficient solution to practical problems. Many general treatises and reviews, as well as increasing number of papers, demonstrate the increasing role of transition metal-catalyzed carbonylations in the field of organometallic synthesis.

Overcoming the fear of the novel type of organometallic reactants and a myth of using “expensive” transition metal complexes in a different way than “classical” organic reagents, some of these systems are used routinely as a tool for the introduction of C = O functionalities of various skeletons of practical importance. The enhanced selectivity, the well-defined mechanism, and the applicability of standard techniques are the main features that make these homogeneous catalytic reactions attractive.

Nowadays, the gap between “organometallic chemists” and those seeking to develop the results (“synthetic chemists”) has been substantially narrowed: most organometallic reagents are used as “tools” in organic synthesis. Both the main-group organometallic chemistry and the transition metal organic chemistry have become indispensable and significant part of the curriculum of the students of chemistry.

As widely known, the earliest step towards organometallic chemistry was done 180 years ago by the synthesis and characterization of the Zeise’s salt (1827). Although several milestones in the development of organometallic chemistry, such as the discovery of biner carbonyls (Mond, 1890), were marked by catalytic significance, the fundamental findings like these remained sporadic in the nineteenth century. At the beginning of the twentieth century, inorganic chemistry was overshadowed by developments in organic and physical chemistry, the developments in both of which laid the foundations for the subdisciplines of coordination

chemistry and organometallic chemistry. The achievements in both fields characterized the chemistry of the second half of the last century.

As far as the application of carbon monoxide as small “building block” is concerned, its history started with the cobalt-catalyzed alkene hydroformylation developed by Roelen in 1939. This seminal work is generally considered as the start of homogeneous catalysis as well. Since then fundamental work of the highest standard has been carried out in homogeneous catalysis featured by several Nobel laureates.

Nowadays, the use of carbon monoxide as a carbonyl source of aldehydes, ketones, carboxylic acids, and their derivatives in various transition metal-catalyzed reactions has become probably the most widespread methodology for homogeneous catalytic reactions. The unbelievably rich chemistry of homogeneous catalysis like carbon–carbon bond forming reactions or hydrogenations of alkenes, alkynes, ketones, oximes or azomethines have also provided products with unprecedented structures. Several known compounds were synthesized by the new synthetic “tools” in acceptable yields, whereas the formation of side products were substantially reduced, that is, the novel methodologies met the environmental requirements. However, since the earliest history of homogeneous catalysis, the highest volume homogeneous catalytic reactions of industrial importance have been the production of *n*-butanal and acetic acid by the rhodium-catalyzed carbonylation of propene and methanol, respectively.

The scope of the book is largely confined to the most recent developments in carbonylation chemistry. Since this book of special focus is not intended to go into the fine details of homogeneous catalysis as well as its historical background, only the most recent achievements of carbonylation chemistry are discussed. I believe there is no need to elaborate further on the earlier findings in view of the excellent textbooks already available. During the last decade, several novel synthetic reactions involving carbon monoxide have been discovered, as well as new methods such as biphasic carbonylation or application of ionic liquids have been developed. It is our purpose to provide a perspective of this formative period through the contributions of the experts on special topics of carbon monoxide activation by transition metals.

Since I am sure that there are several details to be criticized and commented on, I would appreciate if the readers of this book would send their remarks both to the corresponding subchapter authors and to me preferably via e-mail (kollar@ttk.pte.hu).

László Kollár

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## 1

**Bite Angle Effects of Diphosphines in Carbonylation Reactions***Piet W.N.M. van Leeuwen, Zoraida Freixa***1.1****Introduction**

The first two wide bite angle diphosphines, BISBI [1] and Xantphos [2], were introduced with the aim of improving the selectivity for linear aldehyde in the rhodium-catalyzed hydroformylation reaction. For designing Xantphos and related ligands, molecular mechanics methods were used. The concept of the natural bite angle  $\beta_n$ , that is, the ligand backbone preferred bite angle, was introduced by Casey and Whiteker [3], and  $\beta_n$  can be easily obtained by using molecular mechanics calculations. This angle gives the relative magnitudes of bite angles of the bidentate ligands, but it does not predict the angles for X-ray structures for two reasons. First, because the parameter for phosphorus–metal–phosphorus bending, the metal preferred bite angle, is set to zero in these calculations. Second, while parameters for the organic part of the molecules are highly accurate, the parameters involving the metal (for bond stretch and dihedral bending) are inaccurate and variable, but this need not distort the relative order of the ligands. The effect on hydroformylation was fairly well predicted and so was the favorable effect on metal-catalyzed hydrocyanation [4]. The bite angle effect on the activity or selectivity has been studied and reviewed for many catalytic reactions [5–9]. Initially for palladium-catalyzed reactions the results seemed rather capricious, but today these reactions are understood reasonably well [10].

For our study of the effect of (wide) bite angle diphosphines on catalytic reactions, a distinction between two different effects, both related to the bite angle of diphosphine ligands, can be made [5]:

- The first one, which we have called the steric bite angle effect, is related to the steric interactions (ligand–ligand or ligand–substrate) generated when the bite angle is modified by changing the backbone and keeping the substituents at the phosphorus donor atom the same. The resulting steric interactions can change the energies of the transition and the catalyst resting states. In rhodium-catalyzed hydroformylation reactions steric effects dominate [11], although an electronic bite angle effect was observed in one instance [12].