Tetrahedron Vol. 41, No. 24, pp. xiii to xiv, 1985
Pergamon Press Ltd. Printed in Great Britain.

PREFACE

The evolution of new chemical reactions into useful processes requires at least three broad stages: (1) observation of one or more examples of a new reaction; (2) systematic studies with a range of substrates, identification of reactive intermediates, determination of mechanism, and definition of the scope and limitations; and (3) application in problems which demonstrate the power of the new chemistry and ultimately provide the most efficient solutions to important practical problems. For organo-transition metal chemistry generally, the first stage grew rapidly in the 1950s, after recognition of the varied and unique bonding arrangements available between metals and carbon units. Mechanistic understanding has also moved rapidly, beginning strongly in the mid-1960s, until now the selectivity available with organo-transition metal intermediates is usually understandable in terms of an established mechanism or a reasonable series of well-established reaction types. Enhanced or special selectivity is the key feature which makes the organo-metallic reagents very attractive on the list of powerful techniques for organic synthesis.

And yet, with demonstrated unique reactivity and selectivity, organo-transition metal complexes are only slowly becoming used by the organic chemist with a need to prepare a particular compound. The delay can be attributed to several pedagogical and technical factors. The teaching of organo-transition metal chemistry and of its relation to organic synthesis is relatively new. Some of the mechanistic possibilities do not have exact parallels in organic chemistry. In the development of organo-transition metal chemistry, obtaining pure compounds and characterization of reactive intermediates required rigorous experimental technique which acquired its own jargon and special apparatus. There is a myth that the techniques are fundamentally different from the usual organic manipulations. The reagents are often expensive, and catalytic processes are not always developed at the same rate as the definition of the scope and limitations of the basic reaction. The reactions are often demonstrated in clever but impractical expensive syntheses, interesting mainly as an intellectual exercise.

These problems can be solved largely by education. The mechanisms for organo-transition metal chemistry are now seen to fit into a well-defined group. The outcome of a given reaction can usually be predicted from the basic mechanisms more easily than, for example, the outcome of a nucleophilic displacement on an unsymmetrical allylic halide (E1, E2, S_N1, S_N2, S_N2'. . .). The experimental techniques overlap almost completely with those used in organic chemistry and using a reagent in a simple preparative experiment does not require the fully rigorous procedures of the original characterization studies. The need for catalytic processes is probably the most important current limitation on application of organo-transition metal reagents on a large scale. Work needs to be done in this area, but it is proper to develop the stoichiometric procedures first, understand and test them completely, and then add the cycling steps to give efficient catalysis. It is not always necessary that the general process be catalytic; re-cycling can be developed to suit the particular application.

In this Symposium-in-Print, the goal is to show by examples that efficient and often rather complex organic synthesis can be accomplished with organo-transition metal reagents, using fairly standard techniques and following well-defined mechanisms. Some of the examples employ catalytic procedures for the key metal-promoted step, but many do not. The first six papers involve intermediates in which the metal–ligand systems function as simple functional groups, modifying the reactivity and selectivity of the carbon ligand in coupling with another substrate. In general, the substrate is not interacting with the metal in these examples. The metal can make the attached carbon unit either electrophilic or nucleophilic, and can make it easier to remove protons from aromatic rings; the metal–ligand array can also influence regio- and stereoselectivity in delicate and predictable ways. The remaining papers rely on mechanisms which are unique to organo-transition metal systems, and take place when several organic species are held in the coordination sphere. A remarkable number of papers are concerned with cycloadditions of alkenes, alkynes and carbon monoxide, leading to aromatic rings and to cyclopentanones. This may reflect a prejudice on the part of the Guest Editor, but is not surprising considering the importance of such rings in important synthesis targets and in the highly convergent strategies made possible by the transition metal-promoted reactions.

This collection is not intended to be comprehensive; many beautiful applications and powerful general methods have been reported elsewhere and are not represented here. The hope is that this series serves at least to provide examples of synthesis strategies which become possible using organo-transition metal reagents.

M. F. SEMMELHACK
Department of Chemistry
Princeton University
Princeton, NJ 08544,
U.S.A.