

COMPREHENSIVE ORGANOMETALLIC CHEMISTRY

*The Synthesis, Reactions and Structures
of Organometallic Compounds*

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*The Synthesis, Reactions and Structures of
Organometallic Compounds*

Volume 7



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COMPREHENSIVE ORGANOMETALLIC CHEMISTRY

Preface

Although the discovery of the platinum complex that we now know to be the first π -alkene complex, $K[PtCl_3(C_2H_4)]$, by Zeise in 1827 preceded Frankland's discovery (1849) of diethylzinc, it was the latter that initiated the rapidly developing interest during the latter half of the nineteenth century in compounds with organic groups bound to the elements. This era may be considered to have reached its apex in the discovery by Grignard of the magnesium reagents which occupy a special place because of their ease of synthesis and reactivity. With the exception of trimethylplatinum chloride discovered by Pope, Peachy and Gibson in 1907 by use of the Grignard reagent, attempts to make stable transition metal alkyls and aryls corresponding to those of main group elements met with little success, although it is worth recalling that even in 1919 Hein and his co-workers were describing the 'polyphenylchromium' compounds now known to be arene complexes.

The other major area of organometallic compounds, namely metal compounds of carbon monoxide, originated in the work starting in 1868 of Schützenberger and later of Mond and his co-workers and was subsequently developed especially by Hieber and his students. During the first half of this century, aided by the use of magnesium and, later, lithium reagents the development of main group organo chemistry was quite rapid, while from about 1920 metal carbonyl chemistry and catalytic reactions of carbon monoxide began to assume importance.

In 1937 Krause and von Grosse published their classic book 'Die Chemie der Metallorganischen Verbindungen'. Almost 1000 pages in length, it listed scores of compounds, mostly involving metals of the main groups of the periodic table. Compounds of the transition elements could be dismissed in 40 pages. Indeed, even in 1956 the stimulating 197-page monograph 'Organometallic Compounds' by Coates adequately reviewed organo transition metal complexes within 27 pages.

Although exceedingly important industrial processes in which transition metals were used for catalysis of organic reactions were developed in the 1930s, mainly in Germany by Reppe, Koch, Roelen, Fischer and Tropsch and others, the most dramatic growth in our knowledge of organometallic chemistry, particularly of transition metals, has stemmed from discoveries made in the middle years of this century. The introduction in the same period of physical methods of structure determination (infrared, nuclear magnetic resonance, and especially single-crystal X-ray diffraction) as routine techniques to be used by preparative chemists allowed increasingly sophisticated exploitation of discoveries. Following the recognition of the structure of ferrocene, other major advances quickly followed, including the isolation of a host of related π -complexes, the synthesis of a plethora of organometallic compounds containing metal-metal bonds, the characterization of low-valent metal species in which hydrocarbons are the only ligands, and the recognition from dynamic NMR spectra that ligand site exchange and tautomerism were common features in organometallic and metal carbonyl chemistry. The discovery of alkene polymerization using aluminium alkyl-titanium chloride systems by Ziegler and Natta and of the Wacker palladium-copper catalysed ethylene oxidation led to enormous developments in these areas.

In the last two decades, organometallic chemistry has grown more rapidly in scope than have the classical divisions of chemistry, leading to publications in journals of all national chemical societies, the appearance of primary journals specifically concerned with the topic, and the growth of annual review volumes designed to assist researchers to keep abreast of accelerating developments.

Organometallic chemistry has become a mature area of science which will obviously continue to grow. We believe that this is an appropriate time to produce a comprehensive review of the subject, treating organo derivatives in the widest sense of both main group and transition elements. Although advances in transition metal chemistry have appeared to dominate progress in recent years, spectacular progress has, nevertheless, also been made in our knowledge of organo compounds of main group elements such as aluminium, boron, lithium and silicon.

In these Volumes we have assembled a compendium of knowledge covering contemporary organometallic and carbon monoxide chemistry. In addition to reviewing the chemistry of the ele-

ments individually, two Volumes survey the use of organometallic species in organic synthesis and in catalysis, especially of industrial utility. Within the other Volumes are sections devoted to such diverse topics as the nature of carbon-metal bonds, the dynamic behaviour of organometallic compounds in solution, heteronuclear metal-metal bonded compounds, and the impact of organometallic compounds on the environment. The Volumes provide a unique record, especially of the intensive studies conducted during the past 25 years. The last Volume of indexes of various kinds will assist readers seeking information on the properties and synthesis of compounds and on earlier reviews.

As Editors, we are deeply indebted to all those who have given their time and effort to this project. Our Contributors are among the most active research workers in those areas of the subject that they have reviewed and they have well justified international reputations for their scholarship. We thank them sincerely for their cooperation.

Finally, we believe that 'Comprehensive Organometallic Chemistry', as well as providing a lasting source of information, will provide the stimulus for many new discoveries since we do not believe it possible to read any of the articles without generating ideas for further research.

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Compounds of the Alkali and Alkaline Earth Metals in Organic Synthesis

B. J. WAKEFIELD

University of Salford

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44.1 INTRODUCTION

This Chapter is concerned with derivatives of the alkali metals, beryllium, magnesium and the Group IIA metals containing definite carbon-metal bonds. Since the compounds are usually handled in solution the distinction between true organometallic compounds and salts of organic anions is in some cases arbitrary. Such reagents as solutions from β -diketones with sodium ethoxide in ethanol are excluded, but aspects of the reactions of α -metallo-derivatives/enolates of mono-carbonyl compounds are covered.

Organosodium and organopotassium compounds have found limited applications in organic synthesis. Some reactions of organic derivatives of the heavier alkali metals, beryllium, calcium, strontium and barium have been studied, but with very few exceptions they are of little value in organic synthesis. On the other hand, organolithium and organomagnesium compounds are among the most useful and versatile reagents for constructing organic molecules. Their greatest utility is in the formation of carbon-carbon bonds, by 'carbanionic' attack at electron-poor carbon atoms, but they can also be used to form a variety of carbon-heteroatom bonds. They also undergo useful reactions involving bond fission, notably those in which elimination leads to reactive intermediates such as carbenes and arynes. Moreover, the variety of reagents that may be readily prepared, by replacement of halogen or hydrogen by the metal (see Chapters 2 and 4) makes available a range of *nucleophilic* synthetic equivalents of various functional groups that normally possess electrophilic character.

The first part of this Chapter is a survey of the reactions of the organometallic reagents, classified in terms of the new bonds formed and the substrates which may be employed, with a section (44.9) on reactions for which the key step is bond fission. In many cases organolithium and organomagnesium compounds give similar reactions. Some attempt is made to compare them and to assess their relative merits in particular applications, but surprisingly few controlled comparisons have been reported. In general, references to papers giving adequate experimental details are cited as far as possible; references to *Organic Syntheses* are given when they are available.

The second part of the Chapter is a tabulated summary of the types of synthon that can be introduced by means of the organometallic reagents.

Some general references to works relevant to this Chapter are as follows: the alkali metals (mainly lithium),¹⁻⁴ magnesium,⁵⁻⁸ beryllium, calcium, strontium and barium.⁷⁻⁹ In this text frequent reference is made to tabulated information in references 1 and 5, but the other references are useful alternatives.

44.2 FORMATION OF CARBON-CARBON BONDS

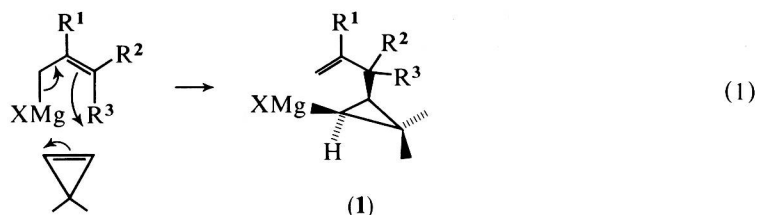
44.2.1 Addition to Carbon-Carbon Multiple Bonds

44.2.1.1 Addition to alkenes and alkynes

Organolithium and organomagnesium compounds are not very reactive towards isolated carbon-carbon multiple bonds, although they do add under appropriate conditions. (Alkylsodium

and alkylpotassium compounds generally metallate alkenes rather than add to them.)¹⁰ Ethene is oligomerized by *n*-butyllithium in the presence of strong electron donors such as DABCO¹¹ and may be trapped surprisingly efficiently by *t*-butyllithium.¹²

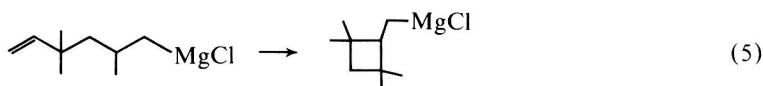
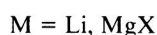
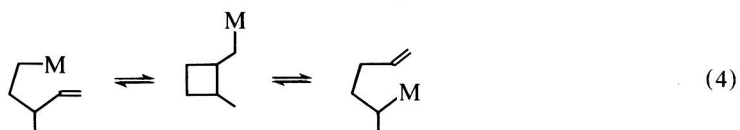
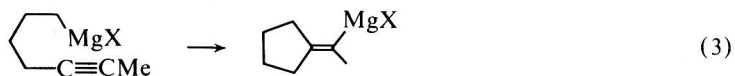
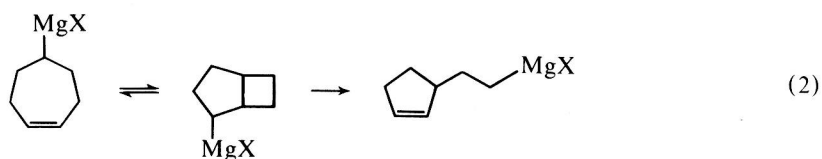
Alkyl lithium compounds and *s*- and *t*-alkylmagnesium compounds add to alk-1-enes under vigorous conditions.^{13,14} Predominantly metal to C-1 addition is observed with the lithium reagents and metal to C-2 with the organomagnesium reagents, but the yields are only moderate because of side reactions. Allylic Grignard reagents are more reactive, and probably add *via* a cyclic transition state (*cf.* equation 1), but the addition is reversible.^{15,16} (Cycloaddition of allylic and azaallylic anions to alkenes is reviewed by Kauffmann.)¹⁷

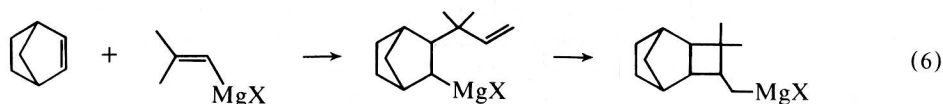


Addition to carbon-carbon multiple bonds occurs more readily under the following circumstances.

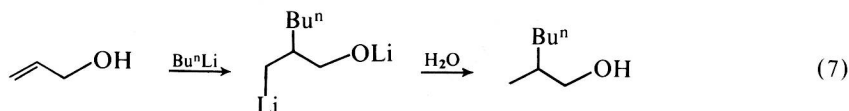
(a) When the multiple bond is strained. For example, alk-2-enylmagnesium halides add stereoselectively to 3,3-dimethylcyclopropene between 0 and 20 °C to give the *cis*-adducts (**1**) *en route* to chrysanthemic acid derivatives.¹⁸ Simple Grignard reagents also add to cyclopropenes.¹⁹ Examples of strained compounds to which addition of an organolithium compound occurs readily include *trans*-cyclooctene²⁰ and a cyclobutadiene.²¹

(b) When addition occurs intramolecularly. Some examples of intramolecular addition to carbene-carbon multiple bonds are shown in equations (2),²² (3)²³ and (4).²⁴ Such reactions have been reviewed.^{25,26} They are of great chemical interest, but their usefulness in organic synthesis is limited by the fact that, as the above examples indicate, they involve equilibria and hence mixtures of products. However, in some cases a useful proportion of one product is present; in the example represented by equation (5) the forward reaction is virtually quantitative at 70 °C.²⁷ It should be noted that cyclization *via* intramolecular addition may follow the addition of allylic magnesium compounds to alkenes, as in equation (6).^{15c}

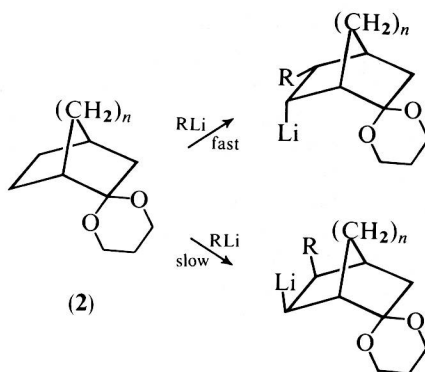




(c) When a suitably placed electron-donating group provides intramolecular assistance. Addition to carbon-carbon multiple bonds is promoted by donor groups such as alkoxy and dialkylamino in allylic or homoallylic positions. For example, allyl- and benzyl-magnesium halides add readily to allyl alcohols.²⁸ Further related examples are referred to in a review, which also describes related transition metal catalysed reactions.²⁹ Alkyl lithium compounds can give useful yields of adducts, as in equation (7).³⁰ Additions similarly occur to propargylic alcohols, amines, *etc.*,^{29,31,32} although with organolithium compounds α -metallation can cause complications.³³



The importance of intramolecular coordination is neatly illustrated by the reactions of compounds (2), where the assisted *endo*-addition is much faster than the unassisted *exo*-addition (Scheme 1).³⁴



Scheme 1

Stereochemical and structural factors influencing additions of dialkylmagnesium compounds to allylic and propargylic alcohols have been studied by Eisch *et al.*³⁵

(d) When the multiple bond bears an activating substituent. Carbon-carbon multiple bonds are activated to addition by various heteroatom substituents and by substituents such as perfluoroalkyl, as well as by conjugative substituents. The reasons for the activation by heteroatom substituents, and the observed regiospecificity of many of the additions, are not always immediately apparent; inductive effects in the ground state and stabilization of the product 'carbanion' may be significant. Nevertheless, the reactions are useful in synthesis, particularly as the substituents may produce *umpolung* of the 'normal' reactivity of the multiple bond. Some examples (including for convenience some substrates with conjugated carbon-carbon multiple bonds) are listed in Table 1. It will be noted that while additions of organo-lithium, -calcium and -barium compounds occur readily, organomagnesium compounds are less reactive. Organomagnesium compounds do react in the presence of nickel(II) salts, and also in some cases under 'Barbier' conditions (*i.e.* by *in situ* reaction of substrate, halide and magnesium).³⁶ An intramolecular reaction of this type (equation 8) has been reported.³⁷

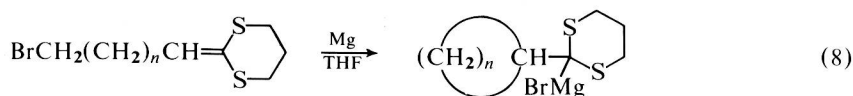

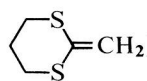
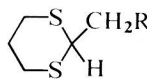
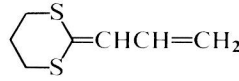
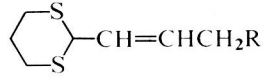
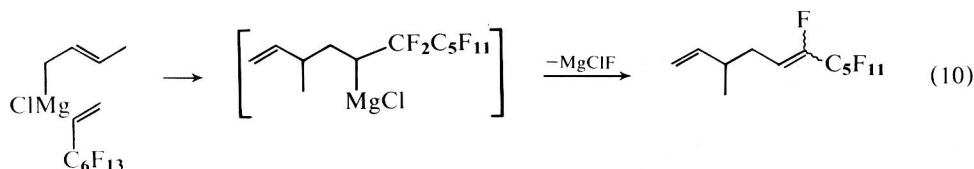


Table 1 Addition of Organo-lithium, -magnesium, -calcium and -barium Compounds to Alkenyl and Alkynyl Derivatives of Second and Third Row Elements

Substrate	Organometallic reagent	Product(s) after hydrolysis	Refs. and notes
$R_3^1SiCH=CH_2$	R^2Li	$R_3^1SiCH_2CH_2R^2$	1
$(R_3^1Si)_2C=CHR^2$	R^3Li	$(R_3^1Si)_2CHCHR^2R^3$	2
$Ph_2PCH=CH_2$	RLi	$Ph_2PCH_2CH_2R$	3
$(PhS)_2C=CH_2$	$(PhS)_2C(Li)Me$		4, 5
	RLi		2, 6
$PhSeCH=CH_2$	RLi	$PhSeCH_2CH_2R$	7
$R_3^1SiCH=CHCH=CH_2$	R^2Li	$R_3^1SiCH=CHCH(R^2)CH_3$	8
	R^2MgX	$R_3^1SiCH_2CH=CHCH_2R^2$	9
	RLi		2
$Me_3SiC\equiv CCH=CH_2$	$PhMgBr$	$Me_3SiC\equiv CCH_2CH_2Ph$	10
	$RCaX, RBaX$	$Me_3SiCH=C=CHCH_2R$	11
		+ $Me_3SiC\equiv CCH_2CH_2R$	
$Et_3GeC\equiv CCH=CH_2$	$RLi, RCaI, RBaI$	$Et_3GeCH=C=CHCH_2R$	12, 13
		+ $Et_3GeC\equiv CCH_2CH_2R$	
$Me_3SiC\equiv CC\equiv CR^1$	R^2Li	$Me_3SiC\equiv CCH=CR^1R^2$	14

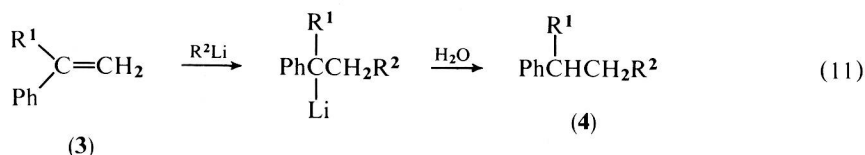
1. See main text ref. 1, p. 95.
2. D. Seebach, R. Bürstinghaus, B.-T. Gröbel and M. Kolb, *Liebigs Ann. Chem.*, 1977, 830.
3. D. J. Peterson, *J. Org. Chem.*, 1966, **31**, 950.
4. T. Cohen, R. B. Weisenfeld and R. E. Gapinski, *J. Org. Chem.*, 1979, **44**, 4744; product formed by cyclization of intermediate $(PhS)_2C(Li)CH_2C(Me)(SPh)_2$.
5. With $PhSCH=CH_2$, addition of RLi is accompanied by metallation: B. Harirchian and P. Magnus, *J. Chem. Soc., Chem. Commun.*, 1977, 522.
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9. V. I. Koshutin, *J. Gen. Chem. USSR (Engl. Transl.)*, 1978, **48**, 1525.
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11. L. N. Cherkasov and O. V. Perepellin, *J. Gen. Chem. USSR (Engl. Transl.)*, 1976, **46**, 2758.
12. M. D. Stadnichuk, *J. Gen. Chem. USSR (Engl. Transl.)*, 1966, **36**, 952.
13. L. N. Cherkasov and M. F. Kozlova, *J. Gen. Chem. USSR (Engl. Transl.)*, 1978, **48**, 1524; L. N. Cherkasov, *J. Gen. Chem. USSR (Engl. Transl.)*, 1976, **46**, 2635.
14. B. G. Shakhovskoi, *J. Gen. Chem. USSR (Engl. Transl.)*, 1969, **39**, 494.

When the multiple bond bears a good leaving group, elimination from the adduct results in overall substitution; the reactions with highly fluorinated alkenes are a well-known example (see Section 44.2.5.1). In some cases, for example equation (9), substitution occurs with rearrangement.³⁸ Elimination from the substituent can also occur, as in equation (10)³⁹ (*cf.* Scheme 71, p. 78).



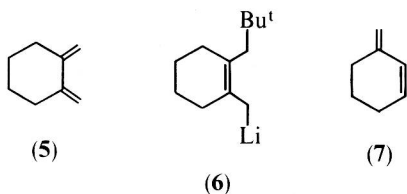
(e) When the carbon-carbon multiple bond is conjugated. Organolithium and organomagnesium compounds add readily to $\alpha\beta$ -unsaturated carbonyl compounds and related systems and, somewhat less readily, to carbon-carbon multiple bonds conjugated with aromatic rings or with other carbon-carbon multiple bonds. The most important examples of the first category — reactions with $\alpha\beta$ -unsaturated carbonyl compounds, imines, and nitriles — are discussed in connection with the reactions with those functional groups. Conjugate addition to $\alpha\beta$ -unsaturated nitro compounds⁴⁰ and sulphones⁴¹ is also potentially useful in synthesis.

The reactions with dienes and arylalkenes are of particular importance in the initiation of polymerization, which is surveyed briefly in Section 44.2.1.2. In some circumstances, however, 1:1 addition (*i.e.* the initiation stage of polymerization) may be accomplished without appreciable further reaction. In the reactions of the organometallic compounds with styrene, propagation is so fast that the initial adducts cannot be usefully intercepted.¹ On the other hand, organolithium compounds add readily to 1,1-diphenylethene (**3**; $R^1 = \text{Ph}$) without polymerization, to give the anti-Markovnikov product (**4**) after hydrolysis (equation 11). With other α -substituted styrenes, *e.g.* (**3**; $R^1 = \text{Me}$), polymerization does occur, but under suitable conditions the adducts (**4**) may be intercepted.⁴² The bis-adducts from *m*-divinylbenzene⁴³ and *m*-diisopropenylbenzene⁴⁴ have been proposed as hydrocarbon-soluble difunctional initiators for anionic polymerization, but some of the claims for quantitative addition without competition from oligomerization have been challenged.⁴⁵ In the reaction of *t*-butyllithium with 1-phenylcycloalkenes, polymerization, allylic metallation and metallation of the phenyl group compete with addition; only in the case of 1-phenylcyclopentene is the adduct the main product.⁴⁶



Addition of organolithium compounds to 1,2-diphenylethene and diphenylethyne occurs, but other reactions detract from its usefulness in synthesis; some of the side reactions probably involve electron transfer.¹

Because of its importance as the initiation stage of polymerization, extensive studies have been made on the addition of organolithium compounds to conjugated dienes, particularly buta-1,3-diene and 2-methylbuta-1,3-diene (isoprene). With *n*-alkyllithium compounds initiation cannot normally be separated from propagation, but with reagents such as *s*- and *t*-butyllithium 1:1 adducts can be obtained in good yields. The regio- and stereo-chemistry of the addition varies with the experimental conditions.¹ In a typical experiment, the reaction of *s*-butyllithium with butadiene in pentane at 35 °C, followed by hydrolysis, gave 5-methylhept-1-ene (11%), *cis*-5-methylhept-2-ene (25%) and *trans*-5-methylhept-2-ene (64%).⁴⁷ Useful evidence that dienes react preferentially in the *s-cis*-conformation is that addition of *t*-butyllithium to 1,2-dimethylenecyclohexane (**5**) gives the adduct (**6**) as the only observable product (by NMR) whereas 3-methylenecyclohexene (**7**) fails to react under similar conditions.⁴⁸



Allylic Grignard reagents give 1:1 adducts with conjugated dienes. Hydrolysis of the adducts gives the dienes formally derived from conjugate addition accompanied by allylic rearrangement, although reaction probably occurs by metal to C-2 addition (Scheme 2). With an excess of the diene, cyclic oligomers are obtained.⁴⁹ Addition occurs under milder conditions with dicyclopentadienylnitrogen dichloride as catalyst.⁵⁰