Synthetic applications of metallate rearrangements

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Abstract - Metallate complexes bearing a 1-hetero-1-alkenyl ligand undergo rearrangment *via* a 1,2-alkyl shift. The reaction generally proceeds with inversion of configuration on displacement of the heteroatom substituent. Metallate complexes of Al, B, Cu, Ni, Zn, and Zr participate in the reaction. The organocuprate reaction provides the first connective and stereoselective synthesis of alkenyl-lithiums and alkenylcuprates from alkylcuprates and metallated enol ether derivatives.

INTRODUCTION

Our aim is to review briefly synthetic applications of carbon-carbon bond forming reactions involving 1-hetero-1-alkenyl metallate complexes 1 in which a carbon ligand R bound to the metal M undergoes a 1,2-shift to an electrophilic carbon attached to the same metal to give an alkenylmetallic product 2. Scheme 1 depicts three of the pathways by which such a transformation might take place. A simple 1,2-shift in the metallate complex 1 with displacement of the heteroatom X can generate the alkenylmetallic 2 directly. Alternatively, interchange of both the R and X groups (a dyotropic rearrangement if the process is concerted) leads to a new metallate intermediate 3 which can transform to 2 on loss of X⁻. Finally, displacement of X⁻ by a pair of electrons from the metal (in the case of transition metals) can lead to an alkylidene carbene 4 which undergoes 1,2-alkyl migration (migratory insertion) to give 2. Special emphasis will be given to synthetic applications of rearrangements of 1 to 2 (M = Cu) discovered at Southampton University in 1988. The review will conclude with a brief consideration of possibly related reactions involving metallate complexes 1 where M = Al, B, Cu, Ni, Zn, and Zr.
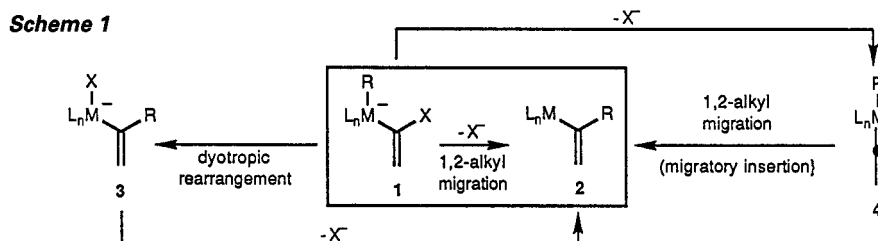
Scheme 1

A NOVEL ORGANOCUPRATE REARRANGEMENT

A key step in our synthesis of the spiroacetal moiety of Milbemycin β₃ (ref. 1) was the nucleophilic scission of the oxiran 5 by the organocuprate 6 (Scheme 2). This was a sluggish reaction which was only made possible by the remarkable thermal stability of the cuprate 6 thereby allowing the reaction to proceed at an appreciable rate at or near room temperature. The resultant intermediate 7 cyclised on treatment with acid to give the desired spiroacetal intermediate 8 in 57% overall yield (5 steps).
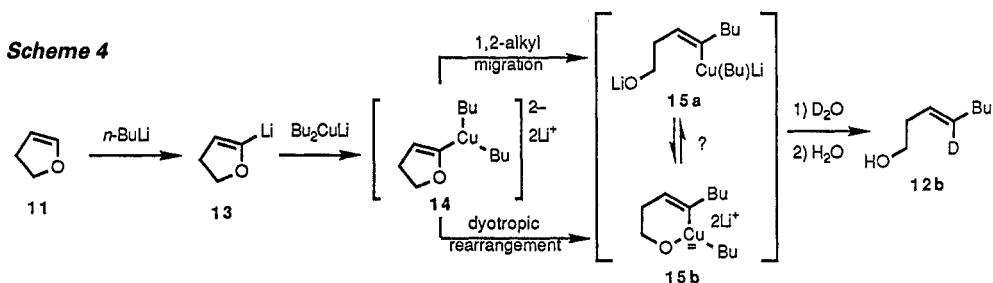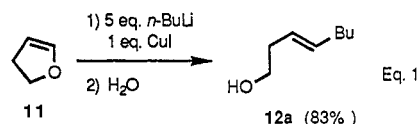
Scheme 2
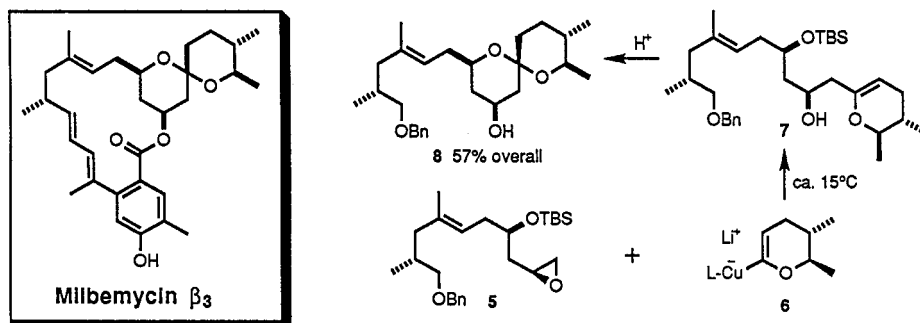
Milbemycin β₃

In retrospect the success of the metallated dihydropyran approacn to Milbemycin β₃ was fortuitous because the corresponding cuprates derived from dihydrofurans and acyclic enol ethers are thermally unstable at the higher temperatures required for reaction with oxirans for

reasons which will be disclosed below.

Another milestone in our exploration of new synthetic chemistry of cyclic enol ethers was the total synthesis of Zoapatanol (ref. 2). Scheme 3 illustrates the early stages of the synthesis in which the enforced geometry of the enol ether 9 in the dihydrofuran ensured the stereochemistry of the trisubstituted alkene in the homoallylic alcohol 10 by virtue of the highly efficient and stereoselective Ni (0)-catalysed coupling of MeMgBr with dihydrofuran 9 (retention). Subsequent investigation of the scope, stereochemistry, and synthetic utility of the Ni(0)-catalysed coupling reaction revealed once again a marked difference in reactivity between dihydrofurans and dihydropyrans as precursors: dihydrofurans react much faster and in higher yield with a wider range of Grignard reagents (ref. 3).

Scheme 3
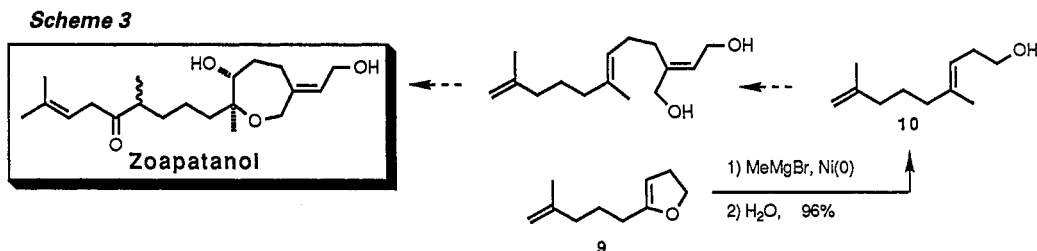
Attempts to circumvent the limitations of the Ni(0)-catalysed coupling reactions led us to examine the superficially analogous Cu (I)-catalysed reaction of organolithium reagents with dihydrofurans described by Sato and co-workers (ref. 4). Thus reaction of dihydrofuran 11 with n-BuLi (5 equiv.) in the presence of CuI (1 equiv.) gave the trans-homoallylic alcohol 12a in 83% yield with high stereoselectivity (Eq. 1). Unlike the corresponding reaction of Grignard reagents under Ni(0)-catalysis (coupling with retention of configuration), the Cu(I)-catalysed reaction appeared to proceed with inversion of configuration. Our investigation of Sato's reaction soon revealed that the Ni(0)- and Cu(I)-catalysed reactions were fundamentally different and that the Cu (I)-catalysed reaction proceeded by a mechanism unprecedented in organocopper chemistry (ref. 5). Three key observations shed some light on the mechanism: (1) 5-alkyl-2,3-dihydrofurans failed to react; (2)

5-lithio-2,3-dihydrofuran reacted with n-BuLi in the presence of Cu(I) to give the same alkenol 12a (>98% E); (3) quenching the reaction mixture with D_2O led to quantitative incorporation of deuterium into C4 of the product. We speculate that the reaction proceeds by a mechanism (Scheme 4) in which 5-lithio-2,3-dihydrofuran 13 is generated under the reaction conditions and this then reacts with lithium di-n-butylcuprate generated *in situ* to form a higher order cuprate intermediate 14 which undergoes a 1,2-alkyl migration or a dyotropic rearrangement (ref. 6) with inversion of configuration to give the lower or higher order cuprates 15a or 15b respectively. These then react with D_2O with clean retention of configuration to give the observed deuterated product 12b.

Scheme 4

Our discovery that metallated enol ethers were necessary reactants in the Cu(I)-catalysed reaction with organolithium reagents suggested a new connective and stereoselective route to trisubstituted alkenes illustrated in Scheme 5. Addition of 5-lithio-2,3-dihydrofuran 13 to a solution of the cyanocuprate generated from n-BuLi gave the higher order cyanocuprate intermediate 17 which rearranged under the reaction conditions to give the putative higher order oxycuprate 18. The latter reacted with allyl bromide to afford the 1,4-diene 12c (R = allyl) as a single isomer in 78% overall yield. Furthermore, 5-(trimethylstannyl)-2,3-dihydrofuran 16 can be used as a substrate in the reaction owing to the precedented transmetallation (ref. 7) of the stannane to the requisite intermediate 17. Quenching with MeI afforded the homoallylic alkenol 12d in 62% overall yield.

Scheme 5
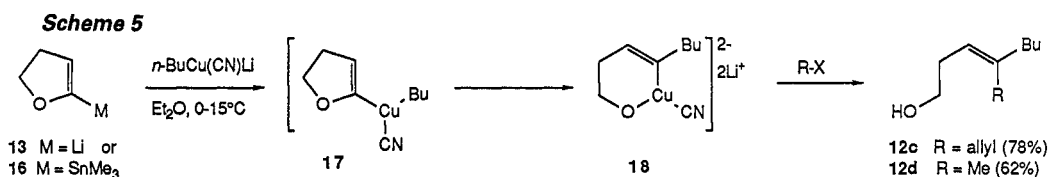
The Cu(I)-catalysed reaction of various organolithium reagents with 13 and the homologous 6-lithio-3,4-dihydro-2H-pyran 19 was examined and the organometallic intermediate quenched with water. As can be seen from the results summarised in Table 1, the reaction

has remarkably broad scope: MeLi, primary, secondary, and tertiary alkyllithiums, PhLi, $CH_2=C(Me)Li$, Me_3SnLi, and $PhMe_2SiLi$ participate in the reaction. With the exception of MeLi, PhLi, and alkynyl-lithiums, the yield of the coupling products is generally good. As little as 2 mol % of CuCN is required to catalyse the reaction when certain organolithium reagents are reaction partners; with Grignard reagents, however, one equivalent of CuCN must be used to get good yields (entries 5 and 10). It is noteworthy that homoallylic organolithiums fail to react whereas the corresponding Grignard reagent works well (entry 10)(ref. 8).

Table I. Cu(I)-Catalyzed Reaction of Organolithium and Grignard Reagents with **13** and **19**.

| entry	α-lithio enol ether	RM (4 equiv)	equiv. CuCN	R (% yield)
1		n-BuLi	0.1	n-Bu (82%)
2		s-BuLi	0.1	s-Bu (88%)
3	**13**	t-BuLi	0.1	t-Bu (77%)
4		o-MeOC$_6$H$_4$Li (1 equiv)	0.5	o-MeOC$_6$H$_4$ (47%)
5		Me$_2$C=C(CH$_2$)$_2$MgBr	1.0	Me$_2$C=C(CH$_2$)$_2$ (75%)
6		MeLi	0.1	Me (52%)
7		n-BuLi	1.0	n-Bu (78%)
8		PhLi	1.0	Ph (25%)
9		CH$_2$=C(Me)Li	0.07	CH$_2$=C(Me) (79%)
10	**19**	PhCH$_2$MgBr	1.0	PhCH$_2$ (60%)
11		PhMe$_2$SiLi	0.2	PhMe$_2$Si (92%)
12		Me$_3$SnLi	0.2	Me$_3$Sn (78%)
13		c-C$_3$H$_5$Li (1 equiv)	0.5	c-C$_3$H$_5$ (33%)

One possible mechanism which accounts for the catalytic nature of the reaction is shown in Scheme 6. According to this hypothesis, the key step in the catalytic cycle is the transmetallation of **13** and **20a,b** to **21** and **22** in which the alkenyl ligand is displaced by the dihydrofuranyl ligand. The inefficiency of the reactions of MeLi (entry 6), PhLi (entry 8), and alkynyllithiums reflects the low migratory aptitudes of methyl, phenyl, and alkynyl ligands leading to competing self-coupling of the enol ether ligands (*vide infra*).
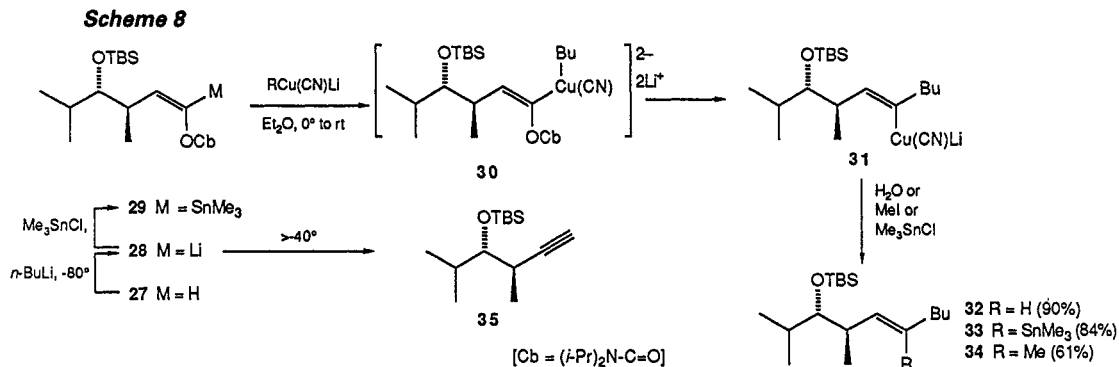
Scheme 6
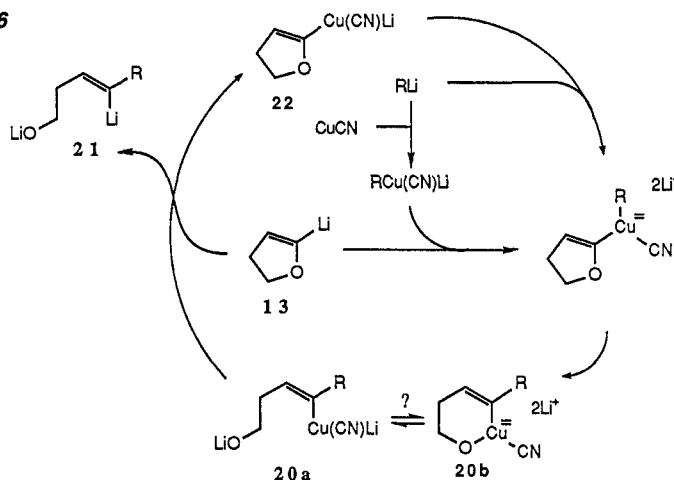
In the absence of an alkyl ligand on copper, lithiated enol enols react with themselves. In the case of dihydrofurans the reaction is fast; dihydropyrans react much more slowly. The course of the reaction and the difference in reactivity can be appreciated by the synthesis of the spiroacetal **26** (Scheme 7). In the presence of only catalytic amounts of CuCN, metallated enol ethers **13** and **23** (derived from reaction of **19** with CuCN) undergo coupling to give the corresponding spiroacetal **26** in *ca.* 64% yield. These experiments shed light on our earlier observation on the instability of cuprates derived from metallated dihydrofurans compared with the dihydropyrans.
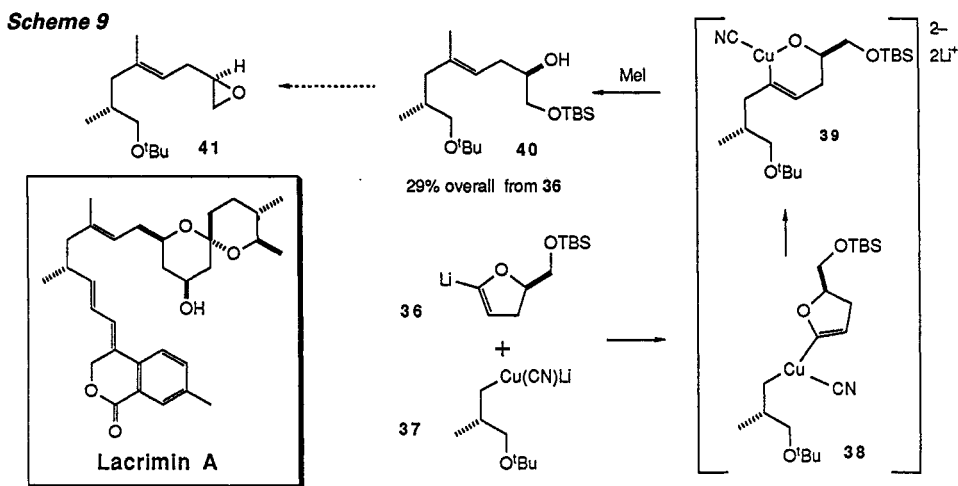
Scheme 7
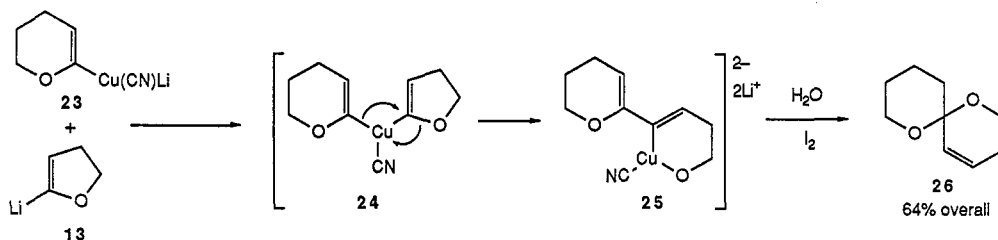
In the search for more reactive partners in our Cu(I)-catalysed 1,2-alkyl migration reactions, we have examined enol carbamates as substrates (Scheme 8). (Z)-Enol carbamates are available with good stereocontrol using the elegant chemistry of Hoppe and co-workers (ref. 9) and they are easily metallated at -80°C with n-BuLi in the presence of TMEDA. Unfortunately, the lithio-derivatives (e. g., 28) undergoes a Fritsch-Buttenberg-Wiechell rearrangement to the acetylene 35 at temperatures above -40°C and so the higher temperatures (ca. 0-20°C) required for the Cu(I)-catalysed 1,2-alkyl migration are inaccessible. However, the requisite higher order cuprate intermediate 30 is generated by transmetallation of the stannane 29 with a lower order cyanocuprate and the desired reaction takes place efficiently to give good yields of the alkenes 32, 33, and 34 after quenching with the appropriate electrophiles (ref. 10, 11).

Scheme 8

SYNTHETIC APPLICATIONS

A synthesis of the antihypotensive agent Lacrimin A (Scheme 9) provided the first significant application of the Cu(I)-catalysed 1,2-migration to natural product synthesis (ref. 12). The trisubstituted alkene in oxiran intermediate 41 was generated by a sequence of reactions beginning with the formation and rearrangement of higher order cuprate 38 from the dihydrofuran 36 and the cyanocuprate 37. The putative oxycuprate 39 was quenched with MeI to give the alkene 40 in 29% overall yield. Since this work was completed, we have found that alternative sources of Cu(I) provide better yields in analogous reactions.
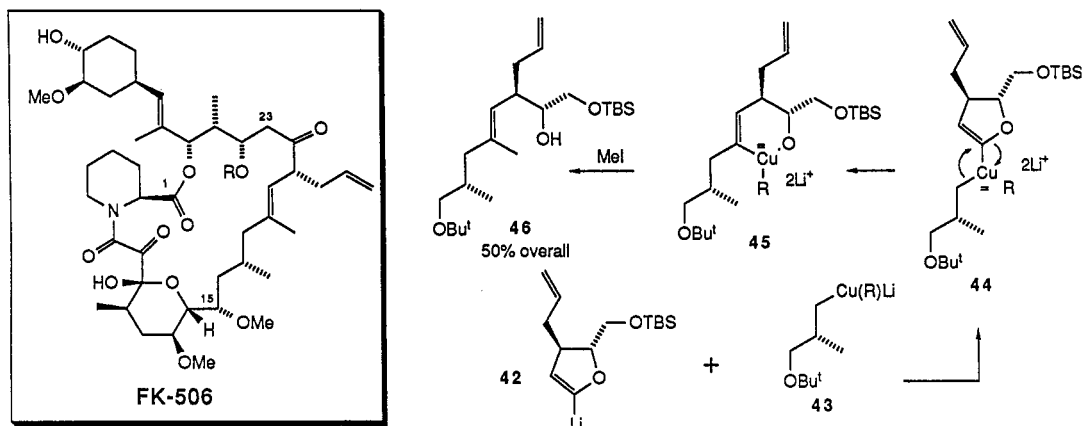
Scheme 9

A synthesis of the C16-C23 fragment 46 of the potent immunosuppressive agent FK-506 (Scheme 10) was efficient and highly stereoselective (ref. 13). Reaction of the lithiated dihydrofuran 42 with the homocuprate 43 in a refluxing mixture of Et$_2$O and Me$_2$S led to formation of the oxycuprate 45 which afforded the desired trisubstituted alkene 46 in ca. 50% overall yield on quenching with MeI in the presence of HMPA. These transformations testify to the value of the method for the construction of trisubstituted alkenes in sterically encumbered environments.

A synthesis of the polyketide fragment 47 of the antifungal cyclodepsipeptide Jaspamide (Scheme 11) demonstrates that dihydropyrans are effective precursors in trisubstituted alkene synthesis (ref. 14).
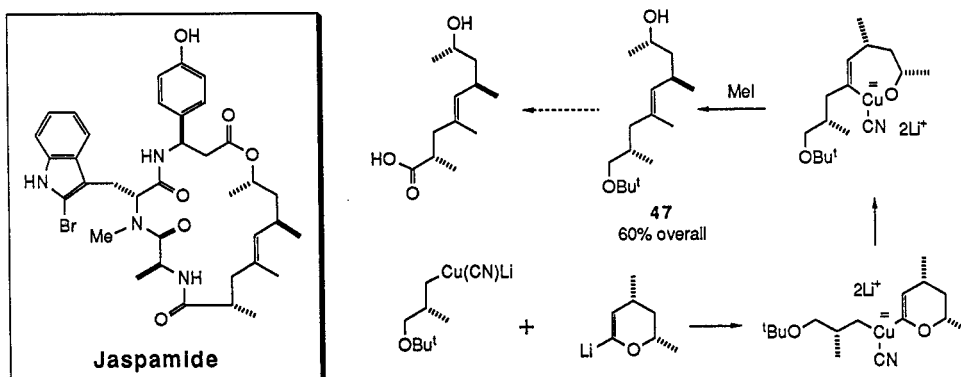
1,2-SHIFTS IN OTHER 1-HETERO-1-ALKENYL METALLATE COMPLEXES

We now wish to set the organocuprate rearrangement described above into context by demonstrating that it is but one example of a general class of 1,2-shifts involving metal and metallate complexes. A variety of heteroarom substituents (nucleofugal groups) and
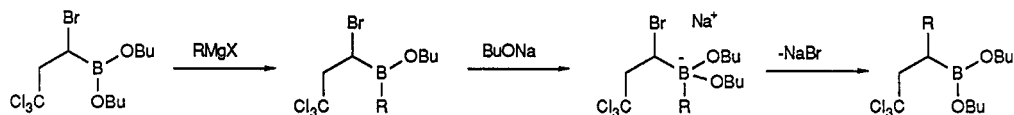
Scheme 10

FK-506

Scheme 11

Jaspamide

metals can participate in the reaction. The prototypical rearrangement involving 1-bromoalkyl borates (Scheme 12) was first described in 1963 by Matteson (ref. 15) and has since evolved into a powerful tool for asymmetric synthesis (ref. 16). More recently, Negishi and co-workers (ref. 17) have established an analogous 1,2-shift of 1-chloroalkyl complexes of Al, Mg, Zn, Cd, Ti, Zr, Hf, V, Cr, Mn, Fe, Co, Ni, and Cu. However, for the purposes of this review we will limit further discussion to 1,2-shifts of 1-hetero-1-alkenyl metallate complexes which bear a closer resemblance to the organocuprate rearrangement under consideration. We begin with examples in which the nucleofugal group is a halogen atom.

Scheme 12

Following the example of Matteson illustrated in Scheme 12, Zweifel and co-workers (ref. 18) showed that the metallate complex derived from treatment of the 1-iodo-1-alkenyl borane 48 (Scheme 13) with NaOMe underwent a 1,2-shift to give the alkoxyborane 49 with clean inversion of configuration. Subsequent protonolysis afforded the trans-1,2-disubstituted alkene 50 in 82% overall yield. Analogous transformations have recently been demonstrated with aluminate complexes (ref. 19).
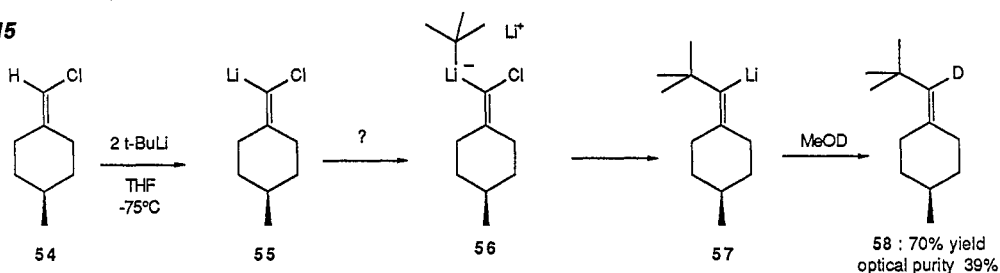
Scheme 13
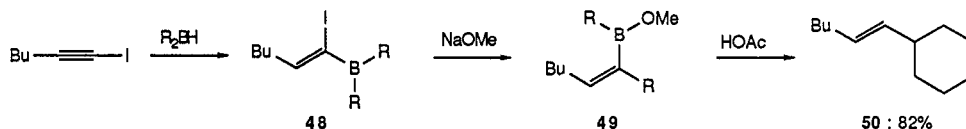
Like the 1,2-shifts described for the trivalent metals boron and aluminium, 1,2-shifts with clean inversion of stereochemistry have also been observed in metallate complexes prepared from the divalent metal zinc (ref. 20). Thus reaction of the vinylidene dibromide 51 (Scheme 14) with Bu_3ZnLi_2 at low temperature yielded the 1-bromo-1-alkenylzincate 52 which rearranged on warming to give the trisubstituted alkene 53 after protonolysis.
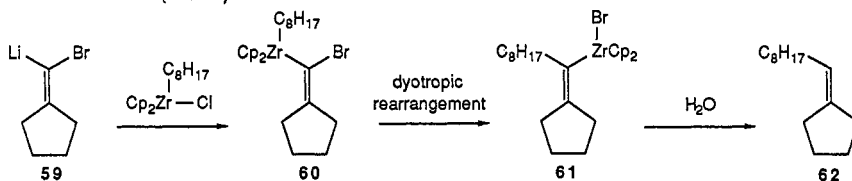
Scheme 14
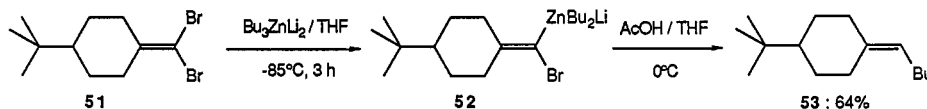
1,2-migration of metallates of monovalent metals may also be possible. Duraisamy and Walborsky (ref. 21) observed that reaction of the optically active chloroalkene **54** with two equivalents of *t*-BuLi produced the optically active deuterated alkene **58** in 70% yield (39% optical purity) after quenching with MeOD (Scheme 15). A bimolecular reaction involving "metal-assisted ionisation" of lithium carbenoid **55** followed by nucleophilic attack by *t*-BuLi was invoked to explain the stereochemistry of the reaction (inversion); however, we suggest an alternative mechanism might involve metallation (retention) followed by formation of the metallate **56** (perhaps as an aggregate) in which intramolecular displacement of the chloride (inversion) occurred *via* an intramolecular process.
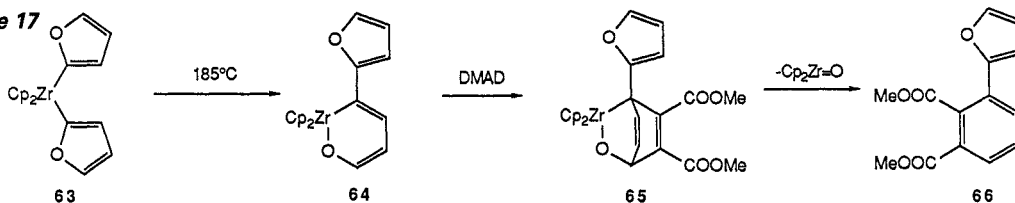
Scheme 15

Organozirconium compounds in which a carbon ligand bears both the metal and a nucleofugal group are known to participate in dyotropic shifts without the intervention of a metallate complex. For example, the alkenyl-lithium **59** (Scheme 16) reacted with *n*-octyl (dicyclopentadienyl)zirconium chloride (ref. 22) to give a 1-bromo-1-alkenylzirconium intermediate **60** which rearranged to alkenylmetallic species **61**. Protonolysis then afforded the observed alkene **62**. Related dyotropic rearrangements in which a phenylthio group serve as the nucleofuge have been described (ref. 23).

Scheme 16

A dyotropic shift involving scission of a furan ring took place on heating the zirconium derivative **63** (Scheme 17)(ref. 24). The intermediate oxazirconocycle **64** was trapped by cycloaddition with dimethyl acetylenedicarboxylate (DMAD) to give an adduct **65** which then underwent cycloelimination of Cp₂Zr=O under the reaction conditions to give the arylfuran **66**. The oxyphilic nature of zirconium explains the driving force for this rearrangement and the high temperature probably reflects the energy required to disrupt the aromaticity of the furan ring.
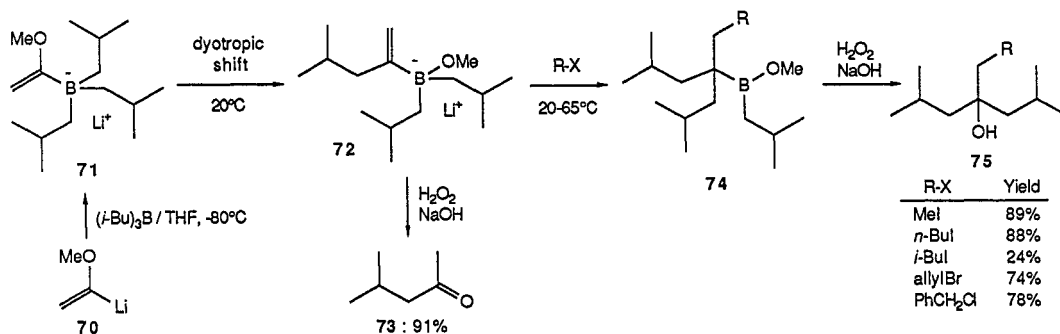
Scheme 17

A copper-catalysed 1,2-shift was observed when 2-furylcopper reacted with iodomethylzinc iodide (Scheme 18). A 1,2-shift of the *gem*-dimetallic intermediate **67** was invoked (ref. 25) to explain the formation of the organocopper reagent **68** which was then alkylated to give the alkene **69** in 74% overall yield. A wide range of organocopper reagents participate in the reaction which establishes zinc carbenoids as efficient a¹/d¹ coupling reagents allowing the sequential linkage of a nucleophile and an electrophile to a methylene group.
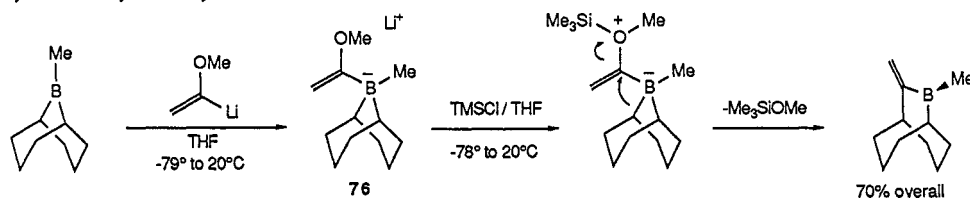
Scheme 18
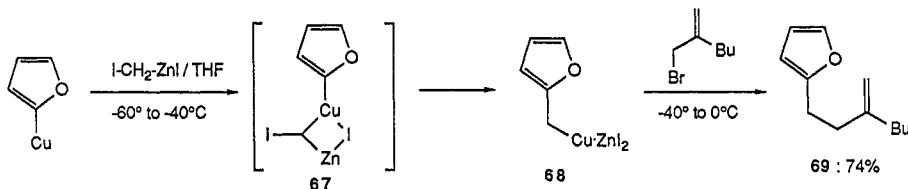
The comparative ease of 1,2-metallate rearrangements wherein halogen serves as the nucleofuge is hardly surprising; rather more remarkable is the fact that alkoxy groups - normally regarded as poor nucleofuges - are also quite readily displaced in 1,2-metallate rearrangements. The first example of such a reaction involving a 1-alkoxy-1-alkenyl metallate was reported by Levy and co-workers (ref. 26) in an organoboron compound. Reaction of α-methoxyvinyl-lithium **70** with (*i*-Bu)₃B (Scheme 19) at low temperature produced the borate complex **71** which underwent a dyotropic shift on warming to room temperature to produce intermediate **72**. Oxidation of **72** with H₂O₂ and NaOH generated the ketone **73** in 91% overall yield. Interestingly, when **72** was heated with various alkyl halides, alkylation of the β-carbon of the alkenylborate took place with concomitant migration of a second *i*-Bu group to produce intermediate **74** which then underwent oxidation to give the tertiary alcohols **75** in good yield. The speed and efficiency of the conversion **72** to **74** indicates that 1-alkoxy-1-alkenylborates are at least as nucleophilic as enamines.

Scheme 19

| R-X	Yield
MeI	89%
n-BuI	88%
i-BuI	24%
allylBr	74%
PhCH$_2$Cl	78%

A more recent investigation in analogous systems (Scheme 20) established that 1-alkoxy-1-alkenylborates such as **76** are stable for prolonged periods at room temperature but that 1,2-alkyl migration is greatly facilitated by Me$_3$SiCl (ref 27). These experiments suggest that the mechanism for the formation of the products observed in Scheme 19 may have to be modified slightly to take into account the apparent stability of 1-alkoxy-1-alkenylborates.

Scheme 20

1-Alkoxy-1-alkenylaluminates display a pattern of reactivity similar to their boron counterparts. Thus the aluminate **77** bearing a dihydrofuranyl ligand (Scheme 21) was unstable and underwent an easy dyotropic shift to the alkoxyaluminate **78** under mild conditions and subsequent protonolysis gave the (*E*)-alkenol **79** (ref. 28). However, the corresponding dihydropyranyl substituted aluminate **80** was stable until challenged by a powerful electrophile in which case a 1,2-alkyl shift was induced without displacement of the adjacent C-O bond.
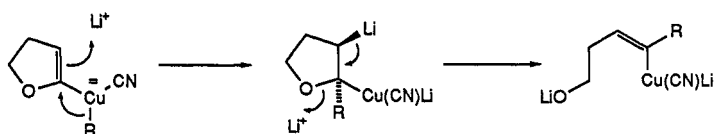
Scheme 21
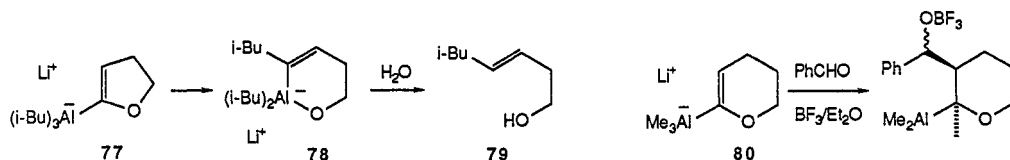
The reaction which bears the closest resemblance to our organocuprate rearrangement was recently reported by Erdelmeier and Gais (ref. 29). Their reaction involved the Ni-catalysed cross coupling between an α-magnesio alkenyl sulphoximine and an organomagnesium reagent to give an alkenyl magnesium derivative. The reaction is exemplified (Scheme 22) by the treatment of the homochiral sulphoximine **81** with 3 equivalents of PhMgBr in the presence of 8 mol% NiCl$_2$(dppp) to give the alkenyl magnesium **83** as a 1:1 mixture of diastereoisomers in 74% yield. Control experiments revealed that the loss of stereochemistry occurred at the initial metallation of the sulphoximine to form **82** and not during the Ni-catalysed cross coupling. Although mechanistic details for this intriguing reaction remain to be established, it suggests that the transition metal-catalysed union of two main group organometallic reagents to generate an alkenyl metal derivative may be a general process.

Scheme 22
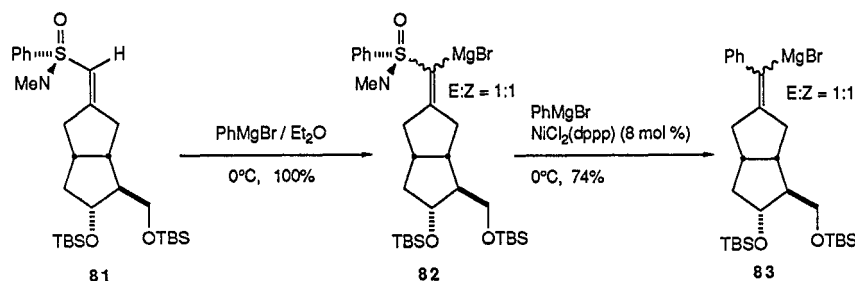
CONCLUSION

We have described a synthetically useful procedure for the stereoselective synthesis of functionalised alkenyl-lithiums and alkenylcuprates. The key step in the sequence, a 1,2-rearrangement of an organocuprate, is a striking example of a significant general class of 1,2-rearrangements displayed by both main group and transition metals bearing 1-hetero-1-alkyl or 1-hetero-1-alkenyl ligands. In the case of 1-alkoxy-1-alkenyl metallates, there are few mechanistic details available and no firm evidence to suggest that all metallates abide by the same mechanism. The simplest mechanisms which accounts for the inversion of stereochemistry observed are a dyotropic shift or a 1,2-migration with simultaneous displacement of an oxygen substituent. An obvious objection to the former is the lack of a convincing driving force for the reaction; the latter requires nucleophilic displacement at an sp^2 centre for which there is meagre

Scheme 23

precedent. The intervention of a vinylidene metallic intermediate (Scheme 1) cannot be discounted though the stereochemistry of the reaction would be difficult to rationalise. The high electron density on the β-carbon of 1-alkoxy-1-alkenylborates and aluminates point to a fourth possibility illustrated in Scheme 23: 1,2-rearrangement induced by electrophilic attack on the π-bond by a lithium cation followed by elimination. We speculate that such a mechanism also accounts for the reaction of n-BuLi with dihydropyran to give alkenol 84 (Scheme 24) (ref. 30) - a reaction for which there has been no previous adequate explanation. In light of the meagre evidence bearing on the detailed mechanism of the rearrangements discussed herein, we suggest that the term 'migratory insertion' previously applied by us and others to both main group and transition metallate rearrangements is neither informative nor accurate and should be reserved for reactions such as transition metal carbonylations and transition metal carbene rearrangements (ref. 31).

Scheme 24
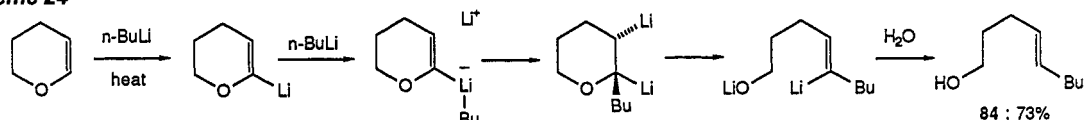
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