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THE INFLUENCE OF COORDINATING SOLVENTS AND COMPLEXING AGENTS ON THE ADDITION REACTIONS OF ORGANOMETALLIC COMPOUNDS

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SUMMARY

The influence of coordinating solvents on the addition reactions of trialkylaluminiums, where the reaction is retarded, and alkyllithium, where reactivity is enhanced, is discussed. Since the mechanisms of the reaction of the two reagents are different, analogies drawn are likely to be misleading.

The addition reactions of trialkyaluminiums with alkenes are inhibited in coordinating solvents. We have recently shown[1] that the reaction of triethylaluminium with 1-octene in diphenyl ether (one of the few which forms a complex weak enough for reaction to be observed) proceeds from the small concentration of uncomplexed monomeric Et_3Al in equilibrium with the complexed species.

On the other hand, it is well known that the addition reactions of alkyllithiums with alkenes are faster in coordinating basic solvents[2–6]. Complexes of alkyllithiums with chelating diamines are reputed to be the most reactive organolithium compounds available[6].

Our mechanism for the reactions of triethylaluminium with alkenes in diphenyl ether solutions has been used as analogy for the reaction of n-butyllithium with ethylene in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA)[5]. We believe argument by analogy is a dangerous principle in organometallic chemistry. The reaction mechanism of a given reagent is liable to change through a series of substrates, as we have observed with triethylaluminium and unsaturated hydrocarbons[7,8]. We are convinced that this particular analogy is a false one. In the case of triethylaluminium, coordinating solvents retard (or suppress) the reaction, because the concentration of the uncomplexed, unassociated reagent (Et_3Al) is depressed by the addition of the solvent (Sv) and the complexed reagent ($Et_3Al \leftarrow Sv$) is unreactive. This explanation cannot be used to explain the *acceleration* of the reactions of butyllithium in the presence of TMEDA. The mechanism proposed[5], that uncomplexed, unassociated reagent (BuLi) is responsible for the reaction, is untenable since its concentration will be depressed in the presence of TMEDA due to the formation of the complex BuLi·TMEDA.

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On consideration of basic reactivities it is difficult to escape the conclusion that the reactive species is a TMEDA complex of butyllithium. It appears probable that there are a number of such complexes and the equilibrium relationships will be most complicated. Only simple cases have been tested so far, or indeed could be tested against the limited kinetic data at present available. There is thus no reason for rejecting the well-established concept of the high reactivity of chelated complexes on kinetic grounds.

The difference of behaviour of alkylaluminium and lithium compounds on the addition of coordinating solvents is not surprising. In the former case it is well-established that the addition reaction with alkenes proceeds through a π-complex in a reaction step which either precedes[8,10] or constitutes[8] the rate-controlling step. This appears to be the only reaction path available when the reaction is an insertion in a covalent metal–carbon bond, and it is obviously not open when the vacant coordination on Al is occupied as is the case in $Et_3Al \leftarrow Sv$. Where the reaction involves a carbanion or paired carbanion, different factors are involved. In general coordinating solvents will increase the concentration of free carbanions and the looser, more reactive ion pairs, thereby increasing the overall reaction rate. This is probably the explanation of the high reactivity of the chelated butyllithium.

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