THE ROLE OF ATE COMPLEXES AS REACTION-DETERMINING INTERMEDIATES*

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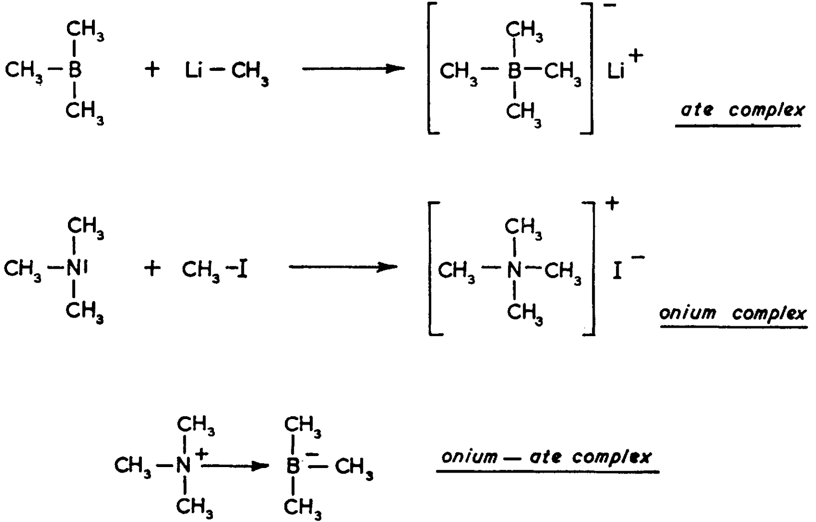
ATE COMPLEXES are diametrically opposed to the familiar onium complexes. Their function as reaction-determining intermediates and as counterparts to the onium complexes has sometimes been inferred or occasionally indicated in the literature, but was first defined by the Reviewer in terms of rigid rules about ten years ago.[1] Little notice has been taken of this generalisation and the term ate complex is generally unfamiliar despite its significance. For this reason this topic is here reviewed.

Although the carbon atom in organic derivatives may expand its valency beyond four only momentarily while passing through the transition state in bimolecular displacement reactions, compounds of elements to the left of carbon in the first row of the Periodic Table can add anionic partners to form negatively charged complexes of varying stability in which the valency of the central atom is increased beyond normal. We call such compounds *ate complexes*, since all the complex anions as in sodium tetraphenylborate or lithium tetracyanoaluminate possess the ending "-ate". These are the counterparts of *onium complexes*, which are formed by elements to the right of carbon by co-ordination with cationic partners and which are positively charged. The following examples illustrate this (Scheme I).



SCHEME I

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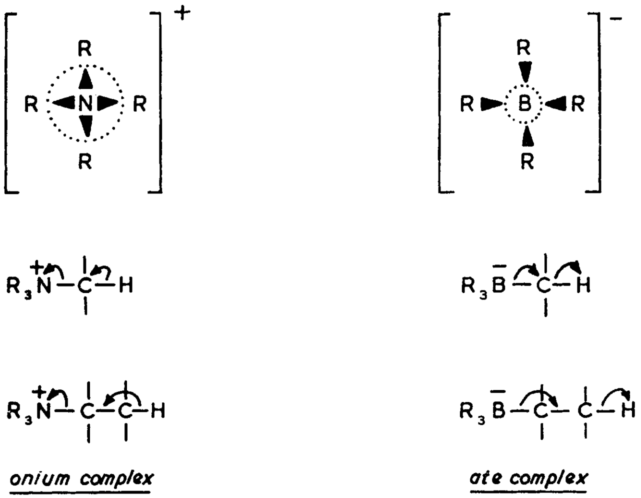
* This Review is based on a lecture given in Sheffield and Manchester in February 1965.

[1] G. Wittig, *Angew. Chem.*, 1958, **70**, 65.

Not only do the majority of the elements qualify for either ate- or onium-complex formation; Lewis acids, as electron acceptors, and Lewis bases as electron donors also unite to form co-ordination compounds which are onium–ate complexes. In order to characterise these classes of compound, the designations ate complexes and onium complexes are precise and clear notations which are acceptable and useful.

Because of the opposing behaviour of onium and ate complexes, these terms imply certain rules regarding their reactivity which allow useful predictions to be made. Whether these rules can be considered general laws only further study can decide. The basic concepts of hydride and proton activation by onium and ate complexes respectively which will form the main theme of this Review are illustrated again using complexes of nitrogen and boron as examples (Scheme II).

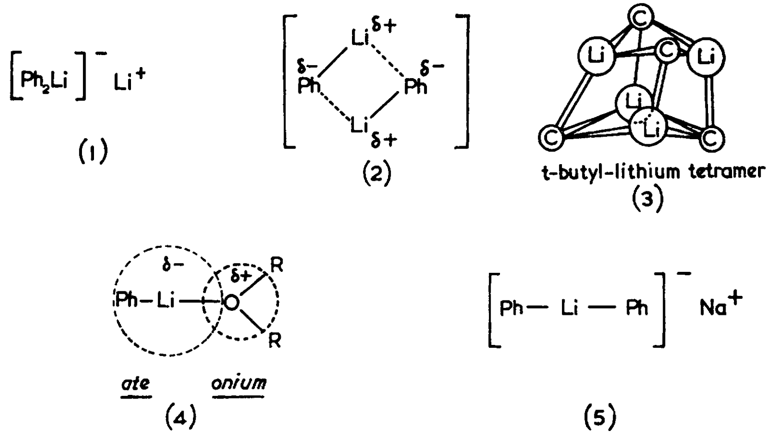


SCHEME II

Complex formation involving either Lewis bases or Lewis acids also influences the nature of the bonding between the ligands and the central atom. In onium complexes all the ligands are *cationically* activated by the inductive effect of the *positive* charge whose geometrical centre resides on the central atom. *Vice versa,* all ligands of ate complexes are *anionically* activated because of the inductive effect of the *negative* charge on the central atom. These inductive effects decrease with increasing distance from the central atom but are powerful enough to mobilise α- and even β-hydrogen atoms as protons in onium complexes or as hydride ions in ate complexes.

As proof of this, the properties of organometallic complexes as static co-ordination compounds, and their dynamics in reactions, are now considered in terms of typical examples.

In the first row of the Periodic Table, the compounds of lithium already exhibit a striking tendency to associate. According to the Reviewer's investigations, phenyl-lithium exists as a dimer over a wide range of concentration. Early on we deliberated whether this dimer in ether is an associated ion-pair in which the lithium cation is held electrostatically as in (1), or whether a four-centre complex such as (2) is present which compares in its bonding with trimethylaluminium.[1,2] Nowadays multicentre type complexes such as (3) are discussed in the literature[3] (Scheme III).



Scheme III

There are probably continuous transitions between the two types of complexes (1) and (2), either extreme being favoured depending on the solvent. Physical measurements show that ethyl-lithium is hexameric and tetrameric in the gaseous state or in non-polar solvents such as cyclohexane. This corresponds fully to the multicentre type complex (3). The fact that organolithium compounds are more reactive in ether than in benzene can be ascribed to solvation of the lithium cation. In ether, co-ordination leads to an onium–ate complex (4), in which competition between the onium and ate functions leads to anionic activation of the phenyl groups as demonstrated by the increase in its nucleophilicity. Eastham's research group in Tennessee[4] found a marked enhancement of the reactivity of butyl-lithium in hexane upon admixture of ether up to a ratio of one mole of ether to two moles of butyl-lithium. The vapour pressure of the ether added is lowered and the dielectric constant of the solution increases significantly, but only until enough ether has been added to form the 2:1 complex.

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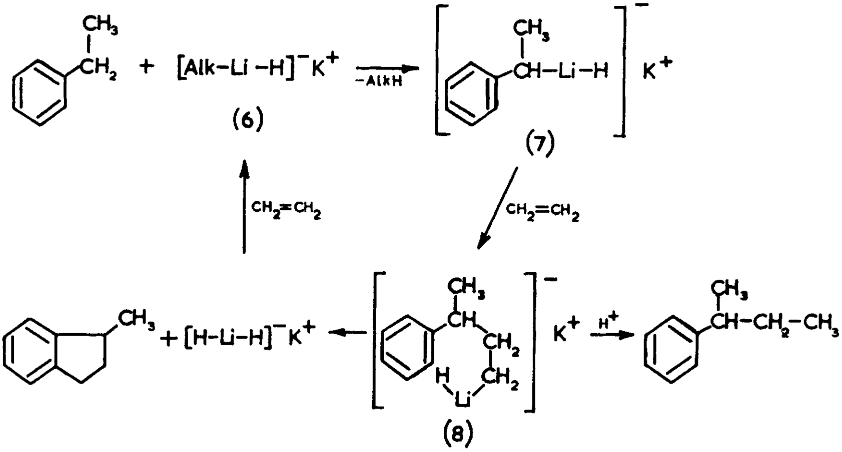
[2] G. Wittig, F. J. Meyer, and G. Lange, *Annalen*, 1951, **571**, 167; G. Wittig, *Angew. Chem.*, 1950, **62**, 231.

[3] M. Weiner, G. Vogel, and R. West, *Inorg. Chem.*, 1962, **1**, 654.

[4] Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *J. Amer. Chem. Soc.*, 1963, **85**, 3517; see also C. G. Screttas and J. F. Eastham, *ibid.*, 1965, **87**, 3276.

In the allied phenyl-lithium–phenylsodium complex, the sodium atom has a lesser tendency to co-ordinate and this favours formation of a complex (5). Our studies again indicated that the phenyl groups in (5) have greater anionic mobility than those in the dilithium complex (1).

In line with these considerations, Eberhardt[5] in Pennsylvania used the complex formed from potassium hydride and butyl-lithium as catalyst for the metallation of ethylbenzene and subsequent alkylation with ethylene (Scheme IV). Neither potassium hydride nor butyl-lithium alone reacts with ethylbenzene, whereas the complex (6) immediately metallates it with generation of a red colour, which may be attributed to the new ate complex (7). The complex (7) in turn adds ethylene to form the next ate complex (8), which now either loses lithium potassium hydride to yield 1-methylindane or is eventually protonated to give s-butylbenzene. Ethylene and lithium potassium hydride regenerate the original catalyst, which is added only in traces. Overall yields of 1-methylindane and of s-butylbenzene of 70% are thus obtained.



SCHEME IV

Our earlier studies[2] indicated that lithium halides *deactivate* organolithium compounds. Phenyl-lithium generated from bromobenzene and lithium in ether is an ionic associate according to molecular-weight determinations; over a small concentration interval it has the same composition as the crystalline adduct consisting of two phenyl-lithium molecules and one lithium bromide that can be isolated from the solution. Although nothing is known about the structure of this complex, the deactivation observed may be ascribed to the fact that lithium bromide is a stronger Lewis acid than phenyl-lithium and thus results in a more stable complex than is obtained by complex formation from phenyl-lithium alone.

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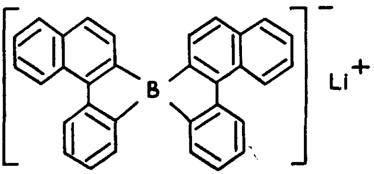
[5] G. G. Eberhardt, *J. Org. Chem.*, 1964, **29**, 643.

Waack and Doran[6] in Massachusetts showed that the polymerisation of styrene initiated by phenyl-lithium is markedly affected by lithium bromide. Since the latter forms complexes with phenyl-lithium, the concentration of free phenyl-lithium is diminished and so is the rate of the initiation reaction. Thus, the ratio of chain initiation to chain growth is shifted in favour of the latter, and consequently the average molecular weight of the polystyrene obtained increased linearly with the lithium bromide concentration.

Passing on from lithium, we observed that the tendency of beryllium or boron to co-ordinate as central atoms with anionic partners is even more pronounced.[2] The stability of the ate complexes increases in the sequence shown here, which is similar to that of the inorganic complex ions. This sequence is due to the increasing valency and hence increasing positive nuclear charge, which holds the anionic phenyl groups with increasing tenacity in the complex sphere (Scheme V).

$$\underset{(1)}{[Ph_2Li]^- Li^+} < \underset{(9)}{[Ph_3Be]^- Li^+} < \underset{(10)}{[Ph_4B]^- Li^+}$$



(11)

SCHEME V

The *spiro*-borate complexes are particularly stable; for example (11) was resolved by Torssell[7] in Sweden into optically active forms, proving the tetrahedral arrangement of the ligands.

The stability of the complexes can be tested by studying their behaviour towards fluorene or benzophenone. Of the complexes mentioned, only phenyl-lithium (1) converts fluorene into the deep orange compound fluorenyl-lithium; the beryllate complex (9) and the borate complex (10) do not react, thus excluding any dissociation of the type (Scheme VI).

$$[Ph_x M]Li \rightleftharpoons Ph_{x-1}M + Ph\,Li \qquad (VI)$$

SCHEME VI

With regard to resistance to hydrolysis, the ate complexes of boron again show the highest stability owing to their complete electron octet,

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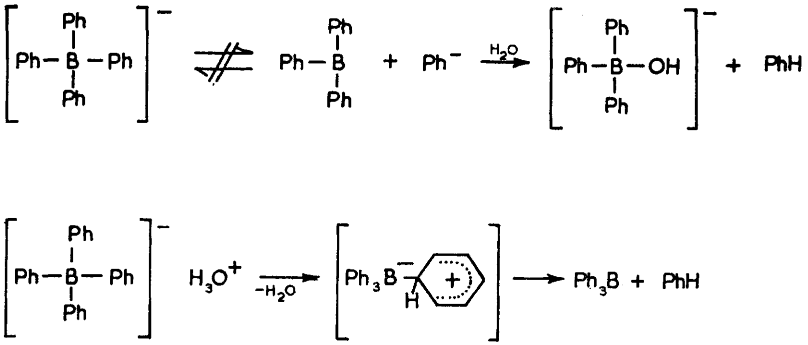
[6] R. Waack and M. A. Doran, *Chem. and Ind.*, 1964, 496.
[7] K. Torssell, *Acta Chem. Scand.*, 1962, **16**, 87.

which is absent from (9). Moreover, in contrast to the central atom in ate complexes of aluminium, boron, because of its small volume, is completely shielded by its four surrounding ligands, thus precluding penetration of anionic reagents such as hydroxide ion to the boron atom. Consequently hydrolysis of the ate complexes of boron should be able to occur only by an S_N1 type of mechanism.



(12) (13)

Scheme VII

It has been shown that tetraphenylborate is *not* subject to such a dissociation, and as expected it is therefore stable in an alkaline medium. On the other hand, it does undergo hydrolysis in an acidic medium (Scheme VII). The hydroxonium–borate complex (12) is only stable for a short time at low temperature in solution. Upon warming, the complex (12) decomposes to triphenylboron and benzene. Potentiometric and kinetic studies by Cooper and Powell[8] in California indicated an electrophilic attack of the proton at the benzene ring, generating the transient zwitterion (13).

The corresponding ammonium salts are more stable than (12). Of interest here is trimethylammonium tetraphenylborate (14), which is stable up to 200°, whereat it decomposes smoothly to trimethylamine, benzene, and triphenylboron, yielding the latter in hitherto unsurpassed purity (Scheme VIII).

Electron-attracting groups such as the cyano-group considerably increase the stability of borate complexes.[9] Thus, a temperature of 100° is required for the hydrolysis with acid of both sodium cyanotriphenylborate and sodium trihydrocyanoborate (15). This demonstrates the countereffect of the cyano-group on the anionic activation in ate complexes. The fact that lithium cyanoboron hydride (15) is so difficult to hydrolyse constitutes an extreme example of this phenomenon. For the same reason,

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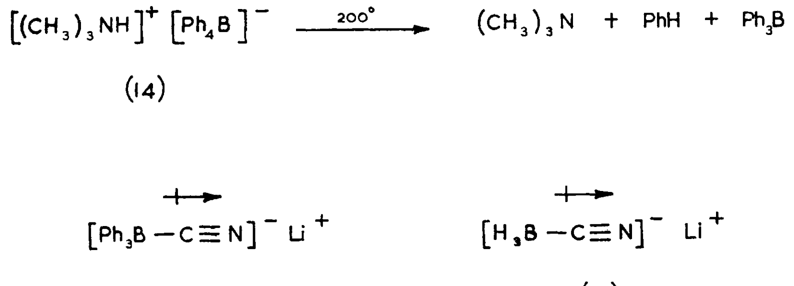
[8] J. N. Cooper and R. E. Powell, *J. Amer. Chem. Soc.*, 1963, **85**, 1590.
[9] G. Wittig and P. Raff, *Z. Naturforsch.*, 1951, 6b, 225.



$$[(CH_3)_3NH]^+[Ph_4B]^- \xrightarrow{200^\circ} (CH_3)_3N + PhH + Ph_3B$$

(14)

$$[\overset{+\!\!\longrightarrow}{Ph_3B-C\equiv N}]^- Li^+ \qquad [\overset{+\!\!\longrightarrow}{H_3B-C\equiv N}]^- Li^+$$

(15)

SCHEME VIII

the reaction of hydrogen cyanide with tetrahydroborate stops at the stage of (15), which is not attacked further by hydrogen cyanide.

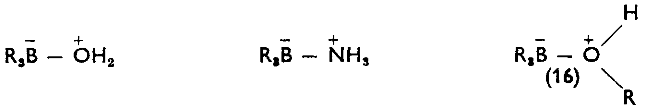
The decrease in stability of ate complexes on changing the central atom from boron to aluminium can also be explained by the considerations already mentioned (Scheme IX). The increasing volume of the central atom leads to a greater distance between the centre of the positive charge and the anionic ligands and also allows hydroxide ions to penetrate more readily through the complex sphere to the central atom, resulting in rapid hydrolysis of aluminate complexes.

$[H_4B]^-Li^+$ $[Ph_4B]^-Li^+$

$[H_4Al]^-Li^+$ $[Ph_4Al]^-Li^+$

SCHEME IX

The anionic activation of ligands in ate complexes and the cationic activation of the ligands in onium complexes explains the behaviour of Lewis acid–Lewis base complexes.



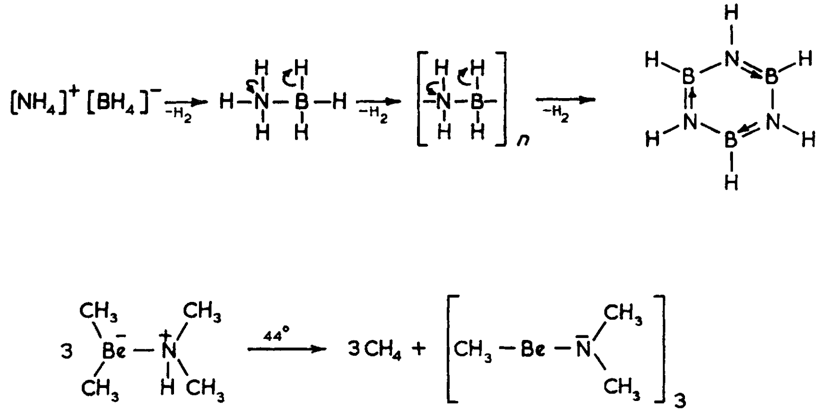
$$R_3\overset{-}{B} - \overset{+}{O}H_2 \qquad R_3\overset{-}{B} - \overset{+}{N}H_3 \qquad R_3\overset{-}{B} - \overset{+}{O}(H)(R)$$

(16)

In the complexes shown here the hydrogen bound to oxygen or nitrogen is distinctly acidic. This is not at variance with our basic considerations, since the deactivation of the proton due to the negatively charged boron is overcompensated by the more direct proton activation by the onium part of the molecule. This explains the increased acidity of alcohols caused by addition of borate esters or aluminium alkoxides discovered by Meerwein.[10] The effect here is so great that the resulting complexes (16) may be titrated as monobasic acids.

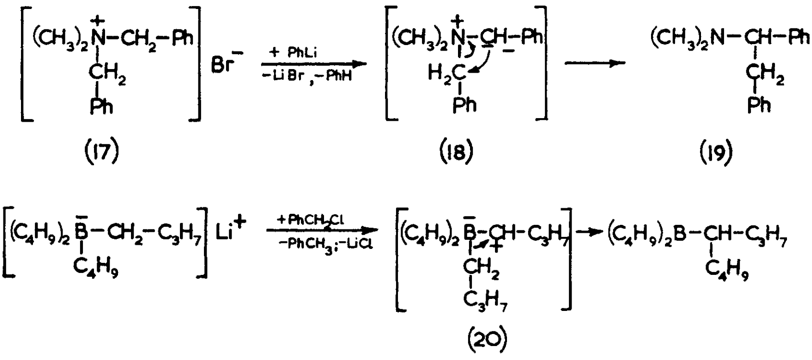
[10] H. Meerwein, *Annalen*, 1927, **455**, 227; H. Meerwein and T. Bersin, *ibid.*, 1929, **476**, 113.

Hydride mobility on the one hand and proton mobility on the other at two *adjacent* atoms account for the conversion of ammonium tetrahydroborate into borazole by heating (Scheme X). A further example of this is the readiness with which methane is eliminated upon heating dimethylammonium dimethylberyllate.[11]



Scheme X

The inverse reactivity of onium and ate complexes is demonstrated impressively in isomerisations which are induced by removal of either a proton or a hydride ion from a complex. The base-catalysed Stevens rearrangement of quaternary ammonium salts is a familiar example. Dimethyldibenzylammonium bromide (17) is converted by phenyl-lithium [presumably *via* the intermediate nitrogen ylide (18)] into the tertiary amine (19)[12] (Scheme XI).



Scheme XI

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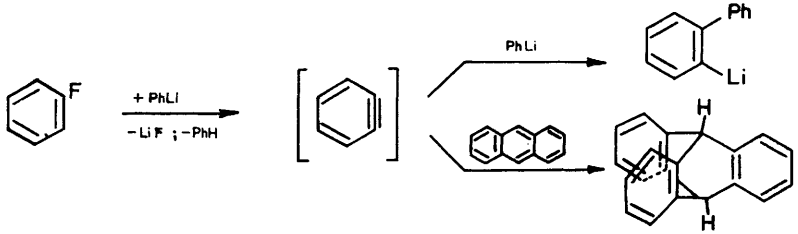
[11] G. E. Coates, P. Glockling, and N. D. Huck, *J. Chem. Soc.*, 1952, 4512.
[12] G. Wittig, *Angew. Chem.*, 1951, **63**, 15.

In this reaction the key step may be formally considered as a migration of the cationically activated benzyl group from the onium complex to the carbanionic site of the ylide. Recently another mechanism was suggested by Jenny and Druey[13] in Switzerland. The counterpart to this reaction in the chemistry of ate complexes is the isomerisation of the boron ylide (20), where the ylide neutralises its charge by migration of an anion from the ate complex to the positively charged site.[14]

Among the penta-aryl compounds of the elements of the fifth group, pentaphenylantimony deserves attention insofar as it adds on phenyl-lithium to form an ate complex (21) with an electron dodecet at the central atom. Lithium hexaphenylantimonate (21) must be in equilibrium with its components, to judge from its ability to metallate the hydrocarbon fluorene. The equilibrium concentration of free phenyl-lithium is naturally very minute, but sufficient to allow the development of a triptycene synthesis based on the dilution principle (Scheme XII).[15]

$$[SbPh_6]^-Li^+ \rightleftharpoons SbPh_5 + PhLi$$

(21)



SCHEME XII

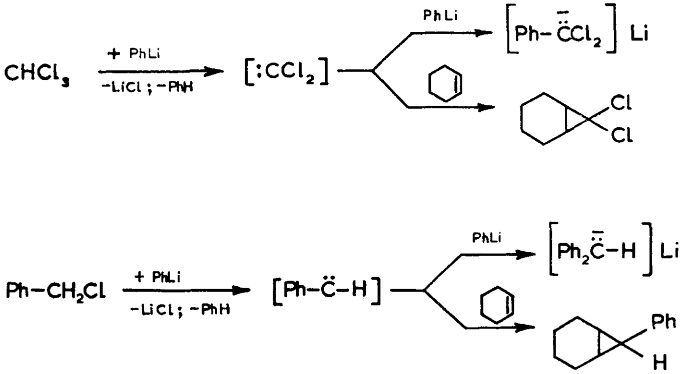
Dehydrobenzene or benzyne can be prepared by the action of phenyl-lithium on fluorobenzene, but dehydrobenzene made in this way adds on phenyl-lithium preferentially even in the presence of excess of anthracene. However, the low stationary concentration of phenyl-lithium in equilibrium with (21) allows the triptycene formation by Diels–Alder addition to become the dominant reaction.

The same principle was used in the reaction of (21) with chloroform or benzyl chloride to afford up to 60% of dichloronorcarane or 15% of phenylnorcarane *via* carbenes which were trapped with cyclohexene[16] (Scheme XIII). Again the concentration of free phenyl-lithium is so small that it does not attack the carbene intermediate.

[13] E. F. Jenny and J. Druey, *Angew. Chem.*, 1962, **74**, 152.
[14] H. Jäger and G. Hesse, *Chem. Ber.*, 1962, **95**, 345.
[15] G. Wittig and E. Benz, *Tetrahedron*, 1960, **10**, 37.
[16] G. Wittig and H. Rabold, unpublished work.

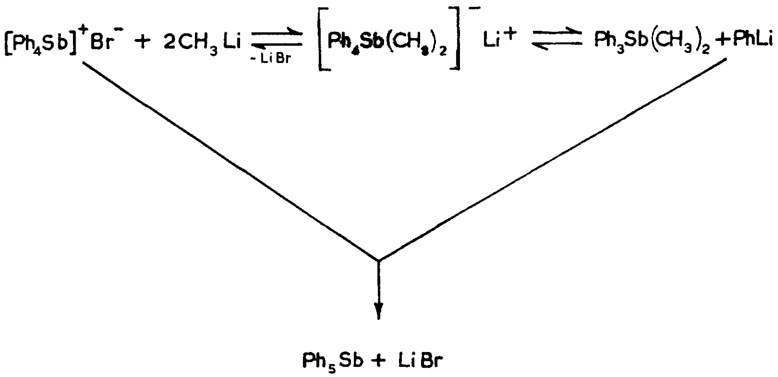
$$[SbPh_6]^- Li^+ \rightleftharpoons SbPh_5 + PhLi$$

(21)



SCHEME XIII

The anionic mobility of the ligands in an ate complex is strikingly documented in some displacement reactions (Scheme XIV).



SCHEME XIV

The reaction of tetraphenylstibonium bromide with methyl-lithium leads to the isolation of pentaphenylantimony owing to the high tendency of the product to crystallise from solution.[17] Wittig and Steinhoff demonstrated recently[18] that when a suspension of pentaphenylantimony is shaken with butyl-lithium in ether ligand exchange again occurs leading *via* ate complexes to pentabutylantimony, which after hydrolysis gave 48 % of a tetrabutylstibonium salt.

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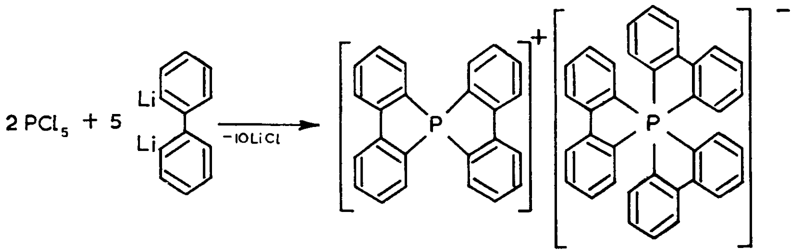
[17] G. Wittig and K. Torssell, *Acta Chem. Scand.*, 1953, **7**, 1293.

[18] G. Wittig and G. Steinhoff, unpublished work.

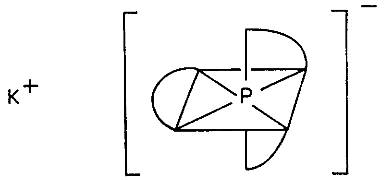
Pentaphenylphosphorane does not form lithium hexaphenylphosphate by addition of phenyl-lithium. Here the ate complex seems to be fully dissociated in contrast to the hexaphenylantimonate considered above. Recently Hellwinkel[19] applied the fact that *spiro*-complexes are more stable to prove that phosphorus is able to form stable ate complexes with six ligands (Scheme XV).



(22)

SCHEME XV

Complex (22) is easy to prepare and is converted by potassium iodide into potassium trisbiphenylenephosphate. This compound can be resolved into its optical antipodes, proving the octahedral structure of this chelate with sexicovalent phosphorus (Scheme XVI).[20]



$$[\alpha]^{24}_{578} = \pm 1930 \quad (c = 0{\cdot}5,\ \text{acetone})$$

SCHEME XVI

Having demonstrated that ate complexes in the series of the fifth group elements may or may not dissociate, we wished to find out whether the stable borate complexes would dissociate for steric or electronic reasons (Scheme XVII). Triptycyl-lithium and triphenylboron unite in an ate complex which is stable even to water.[21] Because of the fixed arrangement of the benzene units in the triptycene part of the molecule, the steric hindrance is not sufficient to enforce dissociation.

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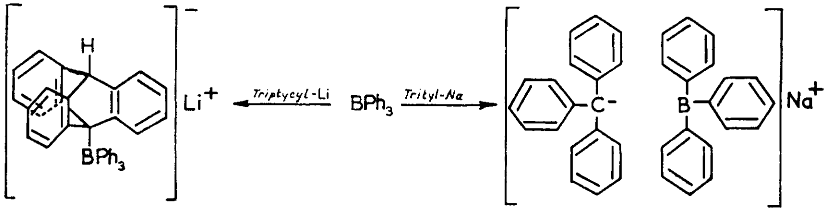
[19] D. Hellwinkel, *Chem. Ber.*, 1965, **98**, 576.

[20] D. Hellwinkel, *Angew. Chem.*, 1965, **77**, 378.

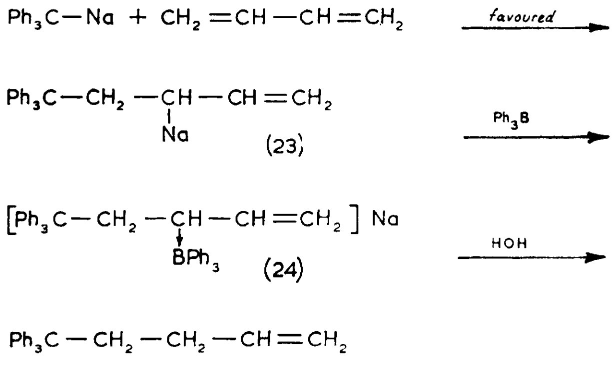
[21] G. Wittig and W. Tochtermann, *Annalen*, 1962, **660**, 23.



SCHEME XVII

Moreover, triptycyl-lithium is not in a position to delocalise the negative charge; this is shown by the fact that triptycyl-lithium is colourless. In contrast, the crystalline 1:1 adduct of triphenylboron and tritylsodium is red. Hence it may be supposed that the boron–carbon bond is not completely covalent, but that the electron pair is delocalised into the phenyl groups of the trityl anion. Because of the increased steric hindrance the two compounds do not unite to form a stable ate complex in solution.

This pair of opposing reagents, tritylsodium and triphenylboron, forms a system which makes it possible to generate new organosodium compounds by the reaction of tritylsodium with suitable partners. The organosodium derivatives are then instantaneously captured by triphenylboron to form ate complexes, as steric hindrance is no longer impeding.



$$Ph_3C{-}Na + CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{\text{favoured}}$$

$$Ph_3C{-}CH_2{-}\underset{Na}{\underset{|}{CH}}{-}CH{=}CH_2 \quad (23) \xrightarrow{Ph_3B}$$

$$[Ph_3C{-}CH_2{-}\underset{BPh_3}{\underset{\uparrow}{CH}}{-}CH{=}CH_2]\,Na \quad (24) \xrightarrow{HOH}$$

$$Ph_3C{-}CH_2{-}CH_2{-}CH{=}CH_2$$

SCHEME XVIII

Polymerisation of butadiene, for instance, can be induced by tritylsodium (Scheme XVIII). In the presence of triphenylboron the first stage, the 1,2 addition product (23), can be intercepted as the ate complex (24), which upon hydrolysis yields triphenylpentene. The ratio of 1,2 to 1,4 additions is a function of the particular Lewis acid used with the tritylsodium.[22]

Triphenylboron not only stops the anionically induced polymerisation

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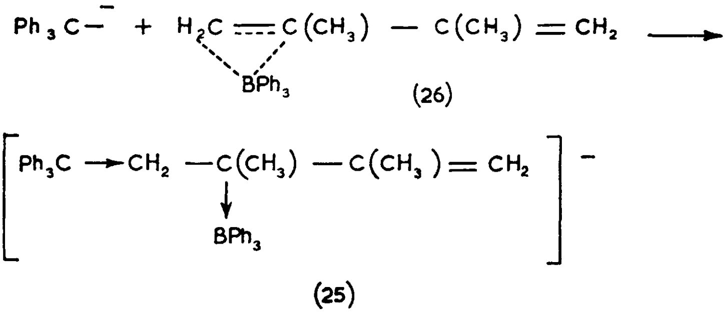
[22] G. Wittig and H. Schloeder, *Annalen*, 1955, **592**, 38; G. Wittig and D. Wittenberg, *ibid.*, 1957, **606**, 1.

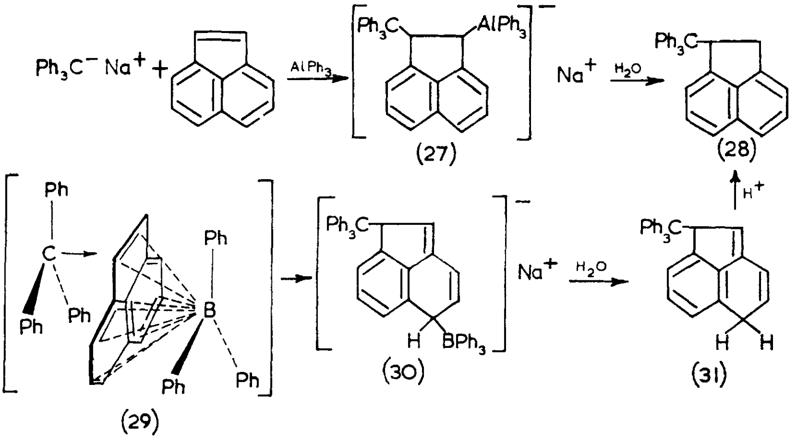
at the first stage, but also accelerates the addition of tritylsodium to the olefin (Scheme XIX).Thus 2,3-dimethylbutadiene is not attacked by tritylsodium alone, but in the presence of triphenylboron addition does occur



Scheme XIX

giving the ate complex (25). The promotion of addition of organometallic agents and the preferred 1,2 addition in the presence of triphenylboron gives insight into the mechanism in that the triphenylboron forms a π-complex (26) with 2,3-dimethylbutadiene. The π-complex (26) is more accessible to nucleophilic attack by tritylsodium since the electron density at carbon atom 1 of the diene is diminished. During the formation of the bond between tritylsodium and carbon atom 1 of (26), the π-complex is transformed into the final product (25), where the triphenylboron is held by a σ-bond at carbon atom 2.

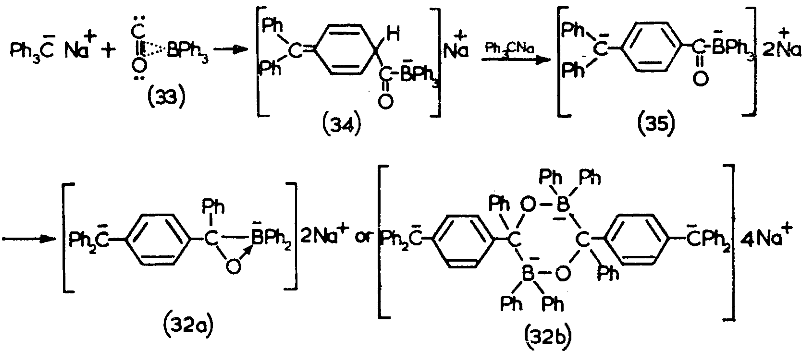
In the polymerisation of acenaphthylene induced by tritylsodium the inhibitors triphenylboron and triphenylaluminium display a selective behaviour (Scheme XX). In the presence of triphenylaluminium, tritylsodium leads to an ate complex (27) resulting from 1,2-addition; after



Scheme XX

hydrolysis, (27) then affords the hydrocarbon (28). In the presence of triphenylboron, however, possibly the ate complex (30) is obtained, *via* the π-complex (29) and a subsequent 1,6 addition. Upon hydrolysis, the complex (30) yields the hydrocarbon (31), whose structure has been clearly established and which can be isomerised to (28).[23]

Thus, tritylsodium, triphenylboron, and 2,3-dimethylbutadiene react only if all three components are present, although no observable reaction occurs with any combination of two of them alone. The same applies to the combination of tritylsodium, triphenylboron, and carbon monoxide.[24] When all three are together, a reaction occurs to form dark crystals that look like potassium permanganate and which dissolve in organic solvents with a deep violet colour. A thorough structural analysis established formula (32) as the probable structure of the complex salt (Scheme XXI). These structures are best reconciled with the following reaction scheme. At the start of the reaction, triphenylboron and carbon monoxide form the π-complex (33) which then reacts with tritylsodium. Electrophilic attack on the latter, which for steric reasons occurs in the *para* position of the phenyl ring, gives rise to the ate complex (34) which is subsequently metallated by tritylsodium yielding (35). An inverse Stevens rearrangement with phenyl migration then affords the final complex (32). It is not yet known whether this "organic permanganate" is monomeric or dimeric, although the dimer is much more likely.



SCHEME XXI

From the wealth of isolable ate complexes of the transition elements, only a few copper complexes will be mentioned. According to Gilman and his co-workers,[25] a suspension of yellow methylcopper in ether dissolves with decolouration upon addition of a second mol. of methyl-lithium, the ate complex lithium dimethylcuprate being formed. The reaction of transition-metal chlorides with 2,2'-dilithiobiphenyl, studied by the Reviewer

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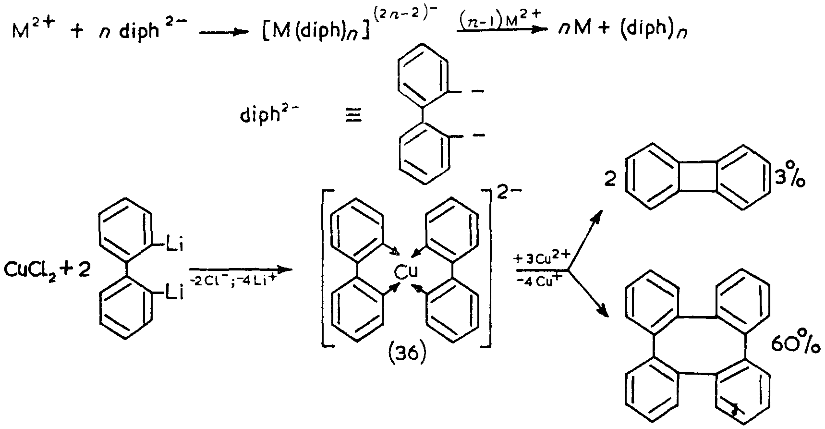
[23] G. Wittig, H. G. Reppe, and Th. Eicher, *Annalen*, 1961, **643**, 47.
[24] G. Wittig, L. Gonsior, and H. Vogel, *Annalen*, 1965, **688**, 1.
[25] H. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, 1952, **17**, 1630.

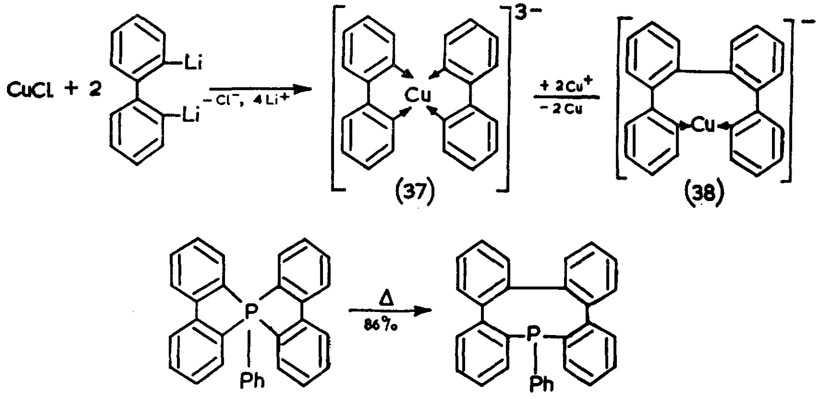
and his co-workers Lehmann,[26] Bickelhaupt,[27] and Klar,[28] generates polyphenylenes and the corresponding acyclic polyphenyls. Condensations up to hexaphenylene and *ortho*-octaphenyl have been achieved.

Ate complexes are also involved here and the number of benzene units in the final product depends specifically on the nature of the metal and is frequently equal to its co-ordination number.



SCHEME XXII

For example, 2,2′-dilithiobiphenyl reacts with cupric and cuprous chloride (Scheme XXII). It reacts with two mols. of cupric chloride to form 60% of tetraphenylene and 3% of biphenylene. These products apparently arise *via* the ate complex (36) by oxidative coupling. The



SCHEME XXIII

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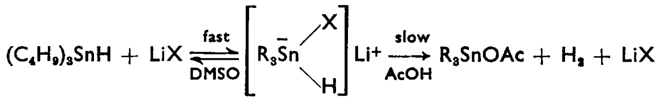
[26] G. Wittig and G. Lehmann, *Chem. Ber.*, 1957, **90**, 875.
[27] G. Wittig and F. Bickelhaupt, *Chem. Ber.*, 1958, **91**, 883.
[28] G. Klar, Dissertation, Heidelberg, 1964.

reaction with cuprous chloride gives the complexes (37) and (38) (Scheme XXIII). The existence of these particularly stable ether-soluble copper complexes can be established by iodolysis; (38) for instance yields 55% of di-iodo-*ortho*-quaterphenyl. Hydrolysis of the reaction mixture gives *ortho*-quaterphenyl as the main product. The by-products are *ortho*-octaphenyl and tetraphenylene formed from (38) by further oxidative coupling. The conversion of (37) into (38) is reminiscent of the almost quantitative thermal isomerisation of *spiro*-phosphoranes to nine-membered cyclic phosphines discovered by Wittig, Maercker, and Hellwinkel.[29]

Reactions in which ate complexes are probably only transient intermediates will now be discussed.

In contrast to carbon, higher elements of the fourth group may expand their electronic shell beyond the octet, thus allowing substitutions to proceed *via* quinquecovalent intermediates. This is a slightly different arrangement from that encountered in the transition states of S_N2 mechanisms where the bond to the incoming nucleophil is formed at the same time as the bond to the leaving group is broken. Recently Dessy, Hieber, and Paulik[30] in Ohio showed that the rate of acetolysis of tributyltin hydride in dimethyl sulphoxide is considerably increased by the addition of lithium halides (Scheme XXIV). This suggests the intermediate occurrence of the ate complexes (39) formed by nucleophilic assistance by expansion of the electron octet. In accordance with our previous considerations, the hydrogen in (39) should have increased hydride character, leading to faster acetolysis. In protic solvents where the nucleophils are deactivated by hydrogen bonding, these effects are, as expected, not observed.



$$(C_4H_9)_3SnH + LiX \underset{DMSO}{\overset{fast}{\rightleftharpoons}} \left[R_3\overset{-}{Sn}\begin{smallmatrix}X\\H\end{smallmatrix}\right]Li^+ \xrightarrow[AcOH]{slow} R_3SnOAc + H_2 + LiX$$

(39)

Scheme XXIV

In the addition of organoaluminium compounds to carbonyl and olefinic double bonds, ate complexes may again be considered as intermediates.[2] The reaction between benzophenone and triphenylaluminium occurs with formation of a distinct yellow colour which disappears rapidly. This excludes a synchronous addition of both reactants and points to a stepwise reaction *via* the ate complex (40), which gives the product by migration of an anionically activated phenyl group (Scheme XXV). Lithium triphenylberyllate (41) is isoelectronic with triphenylaluminium and gives the same reactions and the same colour effect. Since (41) does not dissociate to give phenyl-lithium, this reaction is

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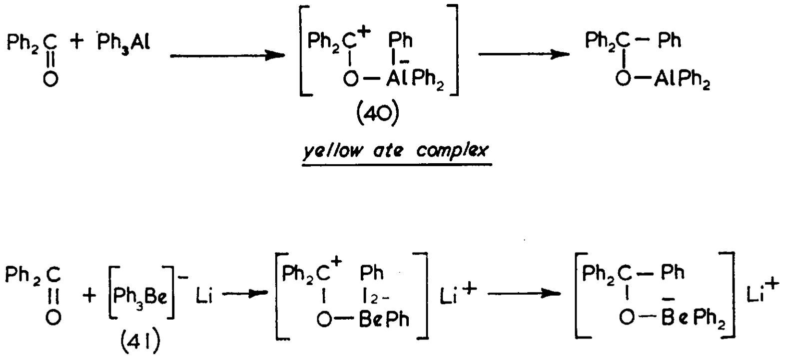
[29] G. Wittig and A. Maercker, *Chem. Ber.*, 1964, **97**, 747; G. Wittig and D. Hellwinkel, *ibid.*, p. 769.

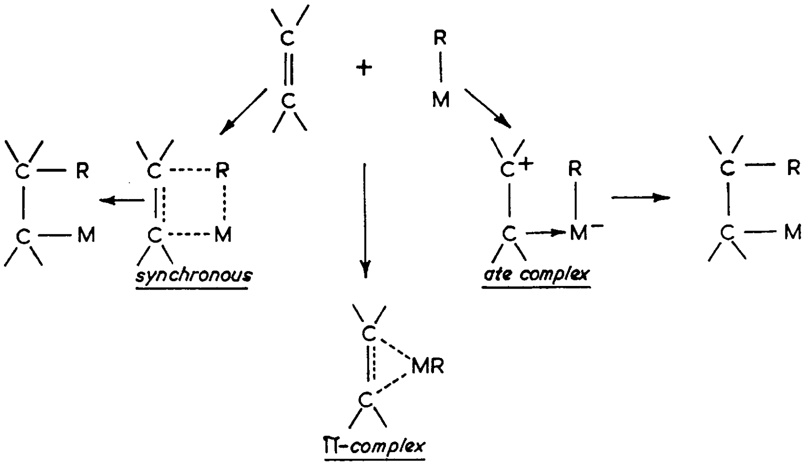
[30] R. E. Dessy, T. Hieber, and F. Paulik, *J. Amer. Chem. Soc.*, 1964, **86**, 28.



Scheme XXV

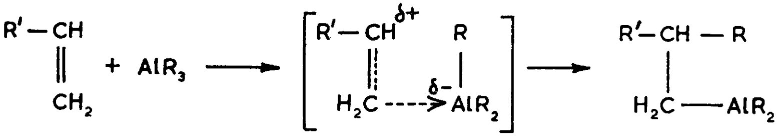
remarkable in that an ate complex not having a complete octet is subject to further co-ordination with a Lewis base.

These examples are members of the large class of addition reactions of organometallic reagents to double bonds. Their mechanism therefore appears to be of fundamental importance.



Scheme XXVI

By analogy with the addition of organometallic reagents to the carbonyl group, it can be discussed whether, for instance, the addition of organo-aluminium compounds to olefinic double bonds proceeds by steps or by a concerted four-centre reaction. According to Dewar, the first step may be assumed to be the formation of a π-complex. This picture is very close to our hypothesis of ate complexes as the first intermediate (Scheme XXVI). As shown already, triphenylboron as a Lewis acid forms a π-complex with non-polarised olefinic double bonds, being oriented midway between the two carbon atoms. The more polar carbonyl double bond will co-ordinate triphenylaluminium preferentially at the more electronegative oxygen atom because of its electron-donor properties. Owing to its charge separation the ate complex obtained will assist inductively in the anionic migration of the ligand to the neighbouring positive atom, with collapse of the energy-rich intermediate. On this basis, it seems reasonable to discuss the action of trialkylaluminium on olefins, which has been studied in detail by Ziegler and his co-workers in Germany[31] along the following lines (Scheme XXVII).



Scheme XXVII

Electrophilic attack of the trialkylaluminium on the double bond results in the formation of the transient ate complex which collapses by anionic migration of the group R to the neighbouring positive carbon atom, yielding a new organoaluminium compound.

Which of the three possibilities, four-centre concerted addition or π- or ate-complex formation, starts the addition process probably also depends on the nature of the metal. Although the tendency to complete the octet shell favours ate-complex formation with aluminium or boron, for instance in hydroboration, organolithium reagents may possibly add *via* a four-centre mechanism. With Grignard reagents the mechanism is even more obscure, as the nature of this reagent is still under debate.

A wide field in which to study these problems is offered by the 1,2 and 1,4 addition of organometallic compounds to $\alpha\beta$-unsaturated carbonyl compounds, but this is beyond the scope of this Review.

That hydrogen atoms in the α- and β-positions to the negative centre of ate complexes are activated as hydride ions has already been demonstrated in the case of ylide formation from lithium tetrabutylborate with benzyl chloride as hydride acceptor.[14] Further instructive examples may now be given.

The reduction of carbonyl groups by triethylaluminium proceeds *via* an ate complex in which the proximity of an electrophilic group to the β-hydrogen favours the hydride shift between the two carbon atoms, affording ethylene and the corresponding secondary alkoxide.[32] The reduction of hindered ketones by Grignard reagents can be formulated in the same manner (Scheme XXVIII).

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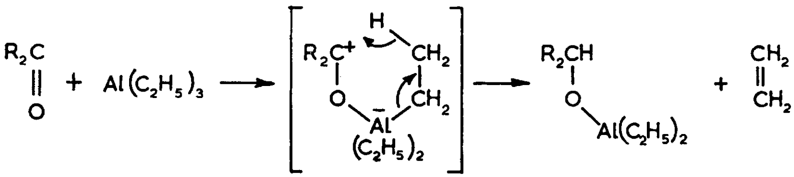
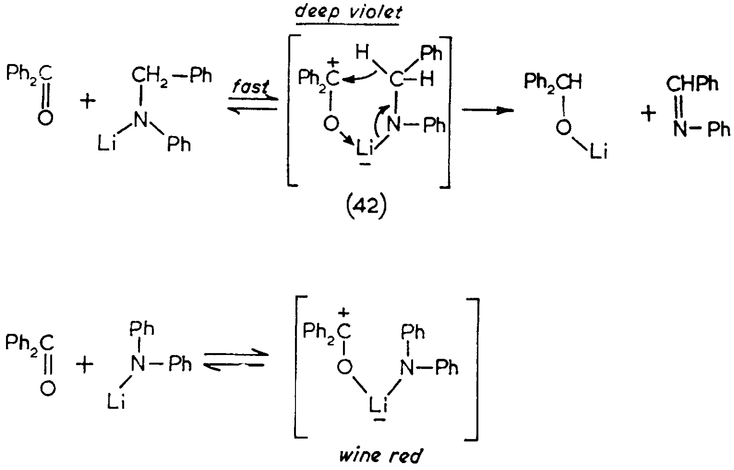
[31] K. Ziegler and his co-workers, *Annalen*, 1960, **629**, 1, and following papers; see also ref. 23.

[32] H. Meerwein, G. Hinz, H. Majert, and H. Sönke, *J. prakt. Chem.*, 1937, (2), **147**, 226.



SCHEME XXVIII

These hydride-transfer reactions in ate complexes similar to the Meerwein–Ponndorf reaction have been studied in more detail in the reduction of benzophenone by lithium *N*-benzylanilide to lithium diphenylmethoxide and benzylideneaniline. The conversion is nearly quantitative and follows second-order kinetics, being of the first order with respect to each partner (Scheme XXIX).[33]



SCHEME XXIX

When the reactants are mixed in ether at 20°, an intense violet colour appears, which fades after a few hours. This colour is ascribed to the ate complex (42), since it is also obtained on mixing benzophenone with lithium diphenylamide in ether. Here a hydride shift is precluded, and hence the wine-red colour persists for days and can be titrated quantitatively with methanol.[34] These observations all indicate the high stability of the ate complex between benzophenone and lithium diphenylamide, which has now even been obtained in crystal form. The reason for its striking deep colour is still unknown, but it may be due to charge-transfer since electron spin resonance measurements show that radicals are not involved.

A last example may serve to recall that ate complexes have their counter-

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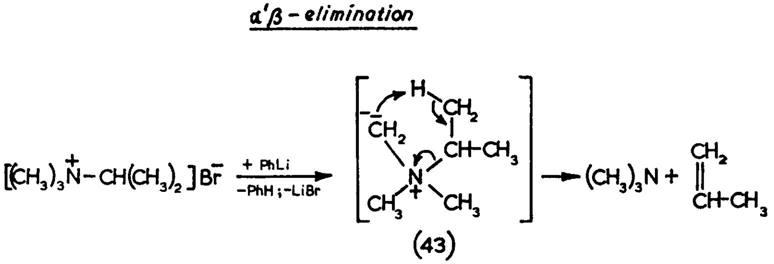
[33] G. Wittig and H. D. Frommeld, *Chem. Ber.*, 1964, **97**, 3541.
[34] G. Wittig and H. Wulff, unpublished work.

parts in onium complexes. In the reductions just mentioned, a hydride ion is transferred within an ate complex. The corresponding proton shift in an onium complex occurs in the $\alpha'\beta$-elimination of ylides (Scheme XXX).



SCHEME XXX

In the ylide (43) formed from isopropyl-trimethylammonium bromide and phenyl-lithium, even the β-hydrogen atoms are activated as protons owing to the inductive effect of the positive charge on the nitrogen, thus facilitating the fragmentation of trimethylamine and propylene.[35]

This Review has demonstrated that a large number of organometallic reactions can be explained in terms of ate and onium complexes. These terms, and the chemistry associated with them are useful for forecasting and detecting new reactions and improving our understanding of known reactions.

[35] G. Wittig and R. Polster, *Annalen*, 1956, **599**, 13; 1958, **612**, 102.