

Ligand Coupling Reactions Through Hypervalent and Similar Valence-Shell Expanded Intermediates

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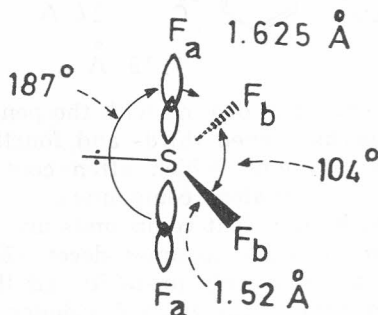
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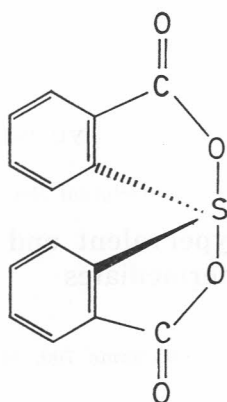
A new concept of ligand coupling reactions through hypervalent and similar valence-shell expanded intermediates is presented with numerous experimental data to support the argument, especially reactions involving the attack of nucleophiles on the tricoordinate sulfur atom.

INTRODUCTION

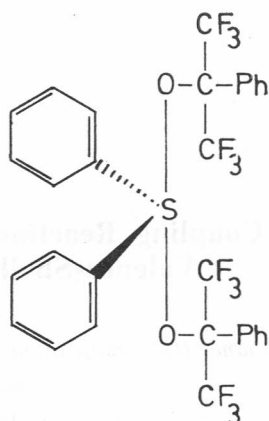
Pentacoordinate phosphorus and sulfur compounds were once considered to assume $3sp^3d$ hybridization.¹ However, a three-centered-four-electron bond, namely a hypervalent bond, containing a p -orbital, was suggested in the early 1950s by Rundle and others^{2,3} for a compound such as SF_4 , the structure of which is shown below.



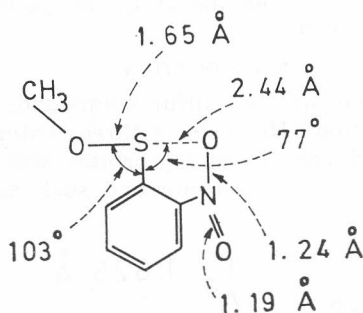
Although the original concept of hypervalency was modified by introducing the participation of $3d$ orbitals into calculation^{4,5} the structural features of the hypervalent compounds have remained nearly the same. For example, two stable sulfuranes, prepared independently by Kapovits et al.⁶ and Martin and his co-workers,⁷ have both two polar and longer S—O bonds nearly at 180° . Even before such stable sulfuranes were prepared, a special weak bonding interaction, namely, hypervalent bonding, was noticed at an extremely short distance between the non-bonding sulfenyl sulfur atom and the oxygen atom of the ortho nitro group in the following compound,⁸ prepared for the X-ray crystallographic analysis. Thus, the distance even between the central divalent sulfur atom and the weakly nucleophilic oxygen atom of the nitro group, together with the linear arrangement of two oxygen atoms and the sandwiched central sulfur atom seem to indicate clearly that such hypervalent bonding is quite common and readily formed.



Kapovits's



Martin's

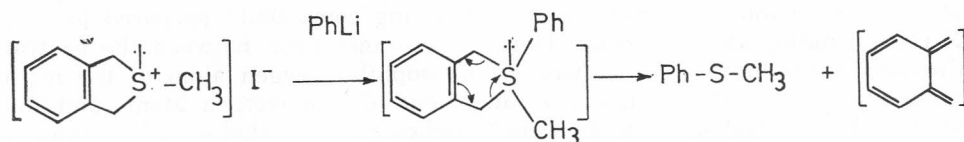


Another important concept in dealing with the pentacoordinate compounds of the second-row and perhaps even third- and fourth-row elements are the pseudo- and/or turnstile rotations, which often control the stereochemistry of the reactions of these hypervalent compounds.

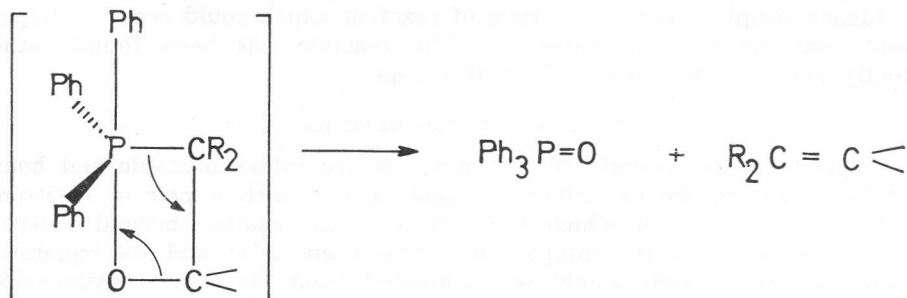
The central atoms in hypervalent compounds are valence-shell expanded; e.g., the sulfur atom in sulfurane assumes decet. Hence, hypervalent compounds or intermediates are relatively unstable and the central valence-shell expanded atom tends to resume the normal valency by extruding a ligand bearing a pair of electrons or a pair of ligands coupled with a pair of electrons. Stable compounds are the ultimate result.

Meanwhile, there are three conceivable ways of hypervalent compounds or intermediates undergoing transformation to stable compounds, in which expanded atom tends to resume the normal valency by extruding a ligand exchange and ligand coupling.

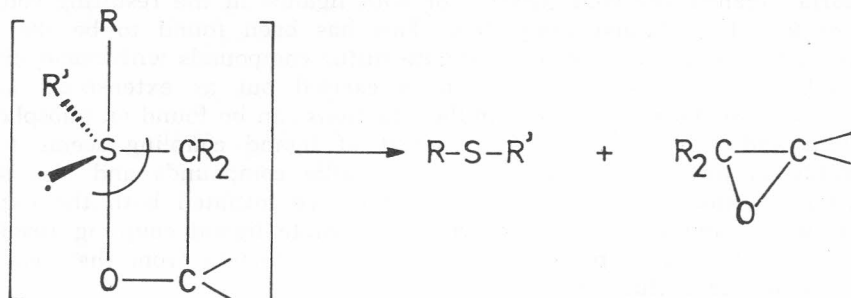
One example of self-decomposition for a sulfurane intermediate may be the following reaction.⁹ Another example may be the Wittig reaction of a



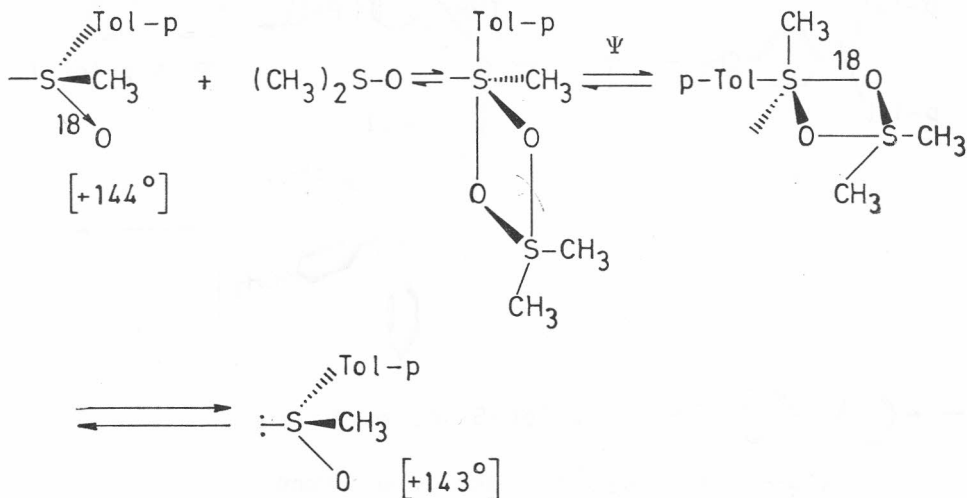
phosphorane, as shown below.¹⁰ In this case, the high energy gained by formation of the P=O bond, ca. 536–578 kJ, would outweigh other possible



reactions. A similar reaction of a typical sulfurane does not proceed in the same manner but undergoes ligand coupling, as shown below,¹¹ probably due to the weak S—O bond of ca. 377 kJ,¹² but affords an epoxide.¹³



Ligand exchange is the best known reaction for hypervalent compounds or intermediates and proceeds either through a typical S_N2 type stereochemical path with configuration inversion in most cases, analogous to the S_N2 type nucleophilic substitution on sp³ carbon atom, or through an intermediate which underwent pseudo-rotation prior to elimination of the withdrawing group, eventually affording a product which retains its configuration.



One of the few examples of the latter case may be the oxygen exchange reactions shown above.¹⁴

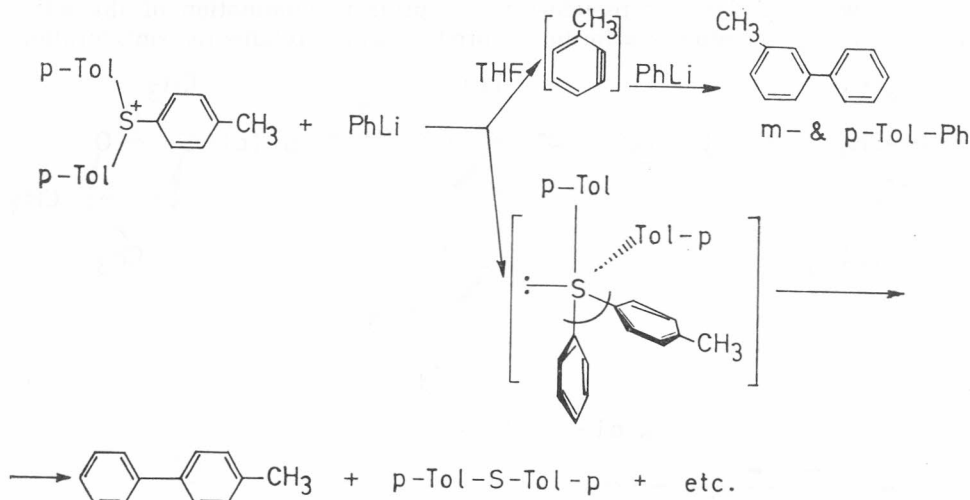
Ligand coupling is the last type of reaction which could occur in hypervalent compounds or intermediates. The reaction has been found rather recently and will be dealt with in this paper.

LIGAND COUPLING REACTION

Hypervalent compounds or intermediates are rather unstable and hence tend to transform, by extruding a ligand or two with a pair of electrons, to stable compounds in which the central atom resumes normal valency. If there is any cohesive interaction between an axial and an equatorial ligand, the two ligands would be eliminated from the central hypervalent atom concertedly giving a ligand coupling product. The main cohesive interaction would result in an overlapping of orbitals of both axial and equatorial ligands. If the coupling reaction proceeds concertedly between axial and equatorial ligands, the configuration of both ligands in the resulting coupled product will be retained completely. This has been found to be the case in one particular reaction of tricoordinate sulfur compounds with nucleophiles. Although stereochemistry has not been carried out as extensively as in the reactions of the sulfur atom, similar reactions can be found on phosphorus, selenium and iodine atoms. This concept of ligand coupling seems to be applicable to many reactions of organometallic compounds and also some oxidation reactions with metal oxides. Thus, we initiated both the experimental works and a literature survey on possible ligand coupling reactions presumed to be taking place on various atoms, starting from the clear cut reactions on the sulfur atom.

A. On the Sulfur Atom

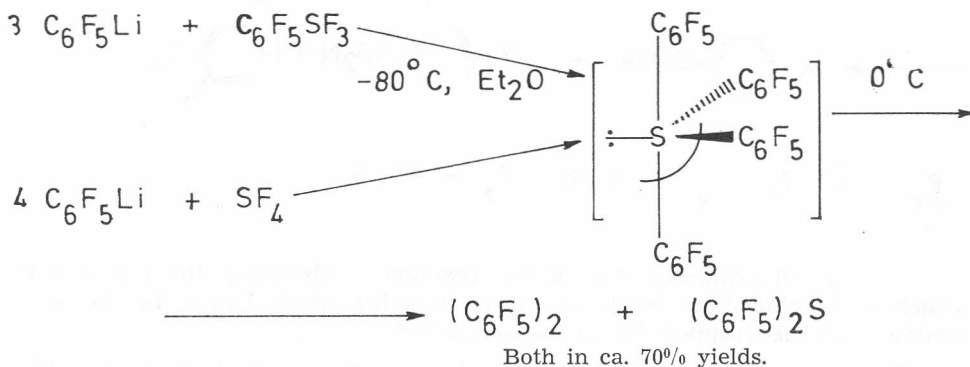
One of the earliest examples is the reaction shown below.^{15,16} Although there were products formed by addition of phenyl- or *p*-tolyllithium an arylene



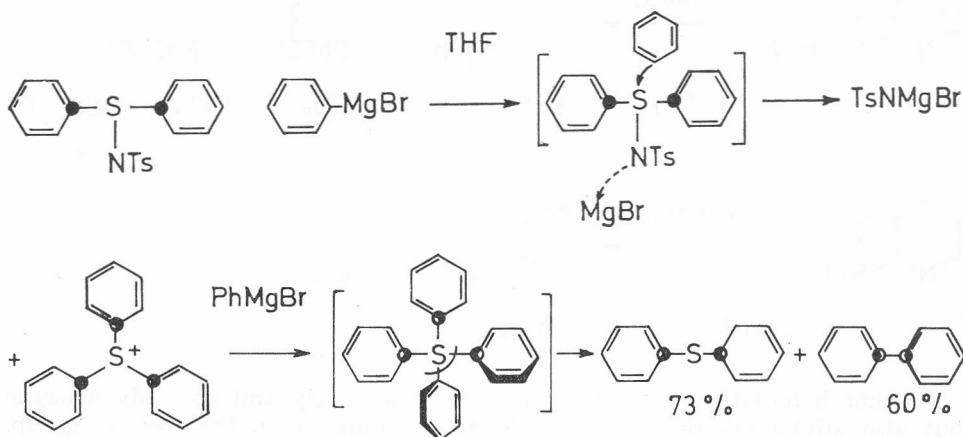
(S⁺ denotes coupling two ligands on S atom)

intermediate, ligand coupling products were obtained in yields of roughly 20%. Under milder conditions, the yields of coupling products were found to increase substantially.^{16,17} Obviously, the overlap of π - or p -orbitals of both equatorial and axial ligands of two aryl groups facilitates the coupling. Meanwhile, by releasing the coupled products with a pair of electrons, the central sulfur atom can resume the valence shell from a decet to a stable octet.

In the following reactions Sheppard observed the NMR spectrum of what seems to be the intervening sulfurane, which, upon warming, gave a perfluorodiaryl coupling product together with di-perfluoroaryl sulfide.¹⁸

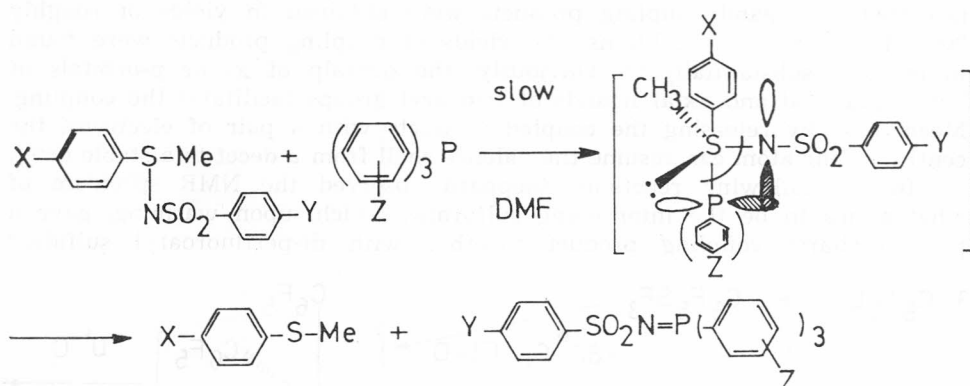


Another example is the reaction between diphenyl *N-p*-tosylsulfilimine and phenylmagnesium bromide, as shown below. Using the ¹⁴C-labelled starting material, diphenyl sulfide and diphenyl were found to have 2/3 and 1/3 of the original ¹⁴C at their ipso positions.¹⁹



Apparently, the ligand coupling took place faster than the pseudo-rotation within the σ -sulfurane, for, if there were faster pseudo-rotations than coupling, the resulting products would contain both 1/2 of ¹⁴C at their ipso positions.

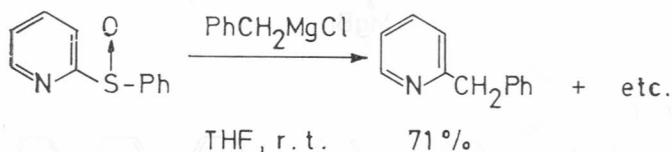
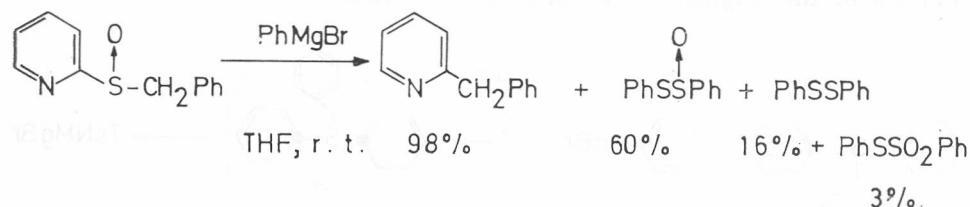
The ligand coupling reaction seems to be more pronounced when the central atoms of the two coupling ligands are heteroatoms of high polarizabilities. One such example is shown below.²⁰



$$f_x = +3.7, \quad f_y = +0.6, \quad f_z = -1.3$$

The rate-determining step of the reaction is obviously the nucleophilic attack of the phosphine, on the tricoordinate sulfur atom. This sulfurane intermediate can be trapped by protic solvents.²¹

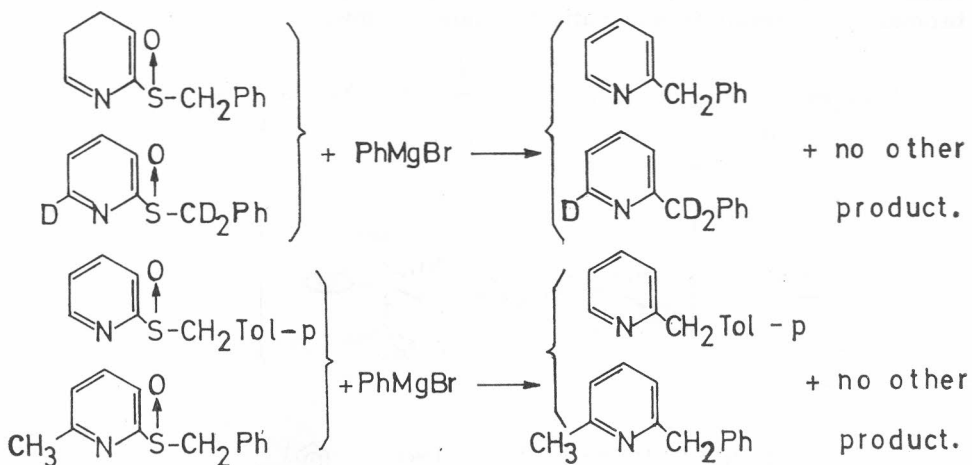
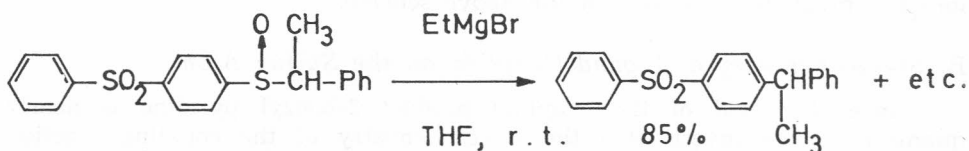
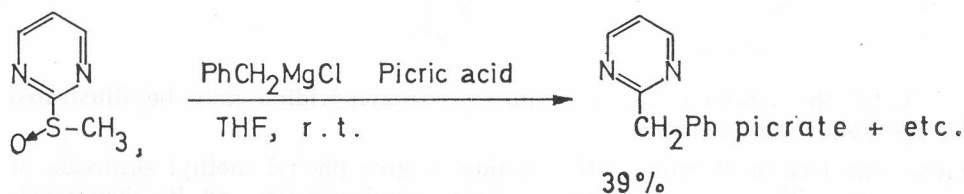
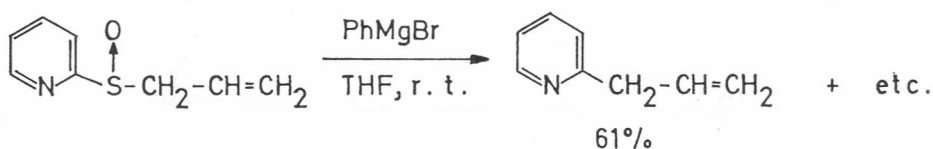
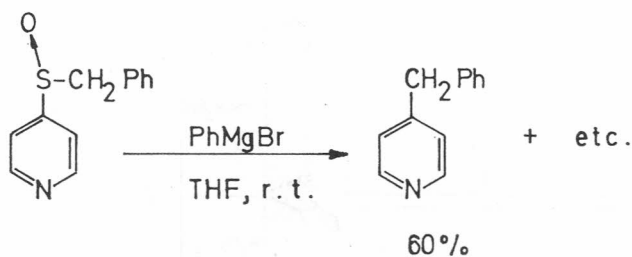
There are many other ligand coupling reactions which proceed within σ -sulfuranes formed upon addition of nucleophiles. The following two reactions are interesting in that in both reactions the coupling product is 2-benzylpyridine.²²



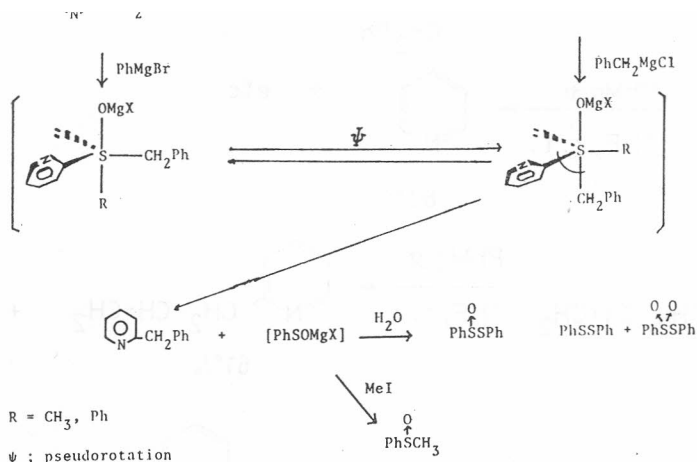
Other heteroatomic sulfoxides also react similarly and not only benzylic but also allylic groups have been found to couple with the pyridyl group, as shown below.²³

The heteroaromatic group can be replaced by an electron-withdrawing aromatic ligand also achieving smooth coupling, as shown in the following reaction.²⁴

On the basis of the following crossover experiments, the ligand coupling reaction has been shown to be exclusively an intramolecular reaction.



When the equatorial ligand, the 2-pyridyl group, and the benzyl group at an axial position undergo coupling concertedly, the remaining organic sulfur intermediate would be PhSOMgX , which can indeed be trapped nicely by

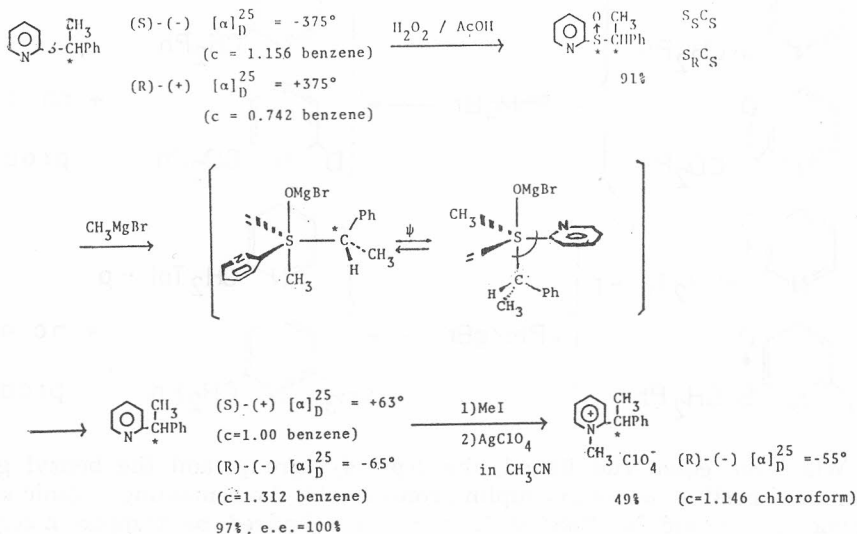


Thus, the ligand coupling forming 2-benzylpyridine may be illustrated in the following scheme.²⁵

either the treatment with methyl iodide to give phenyl methyl sulfoxide or quenching with water to afford diphenyl thioisulfinate and its disproportionation products, as shown in the above scheme.

B. Stereochemistry of Ligand Coupling on the Sulfur Atom

Since the yield of the coupling product 2-benzyl pyridine is nearly quantitative, we investigated the stereochemistry of the coupling reaction using optically active 1-phenylethyl 2-pyridyl sulfoxide with methylmagnesium bromide. The result is schematically shown below.

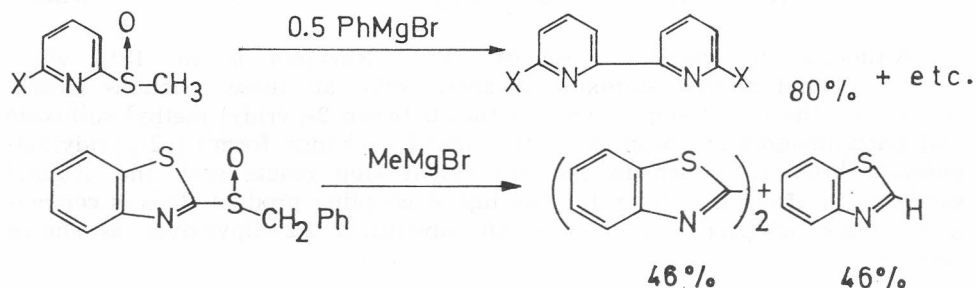


As the (S) isomer was converted to the crystalline *N*-methyl perchlorate for X-ray crystallographic analysis, it was concluded that the reaction had taken place with a complete retention of configuration.²⁶

This stereochemical experiment clearly shows that the ligand coupling within the σ -sulfurane is a concerted process.

C. Ligand Coupling and Ligand Exchange on the Sulfur Atom

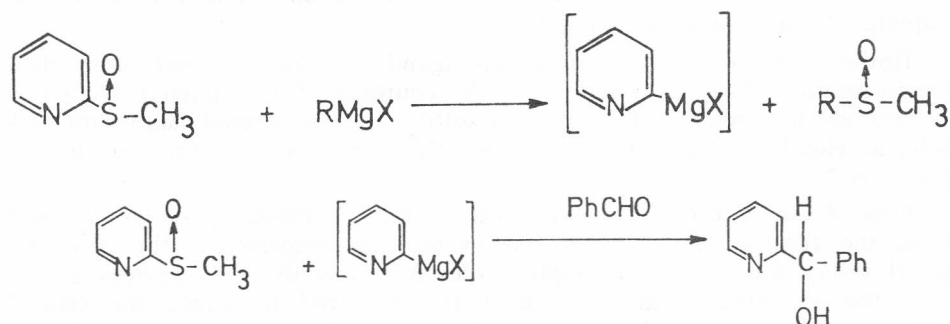
There are cases in which ligand exchange and ligand coupling take place consecutively, both through σ -sulfuranes. One example is shown below.²⁷

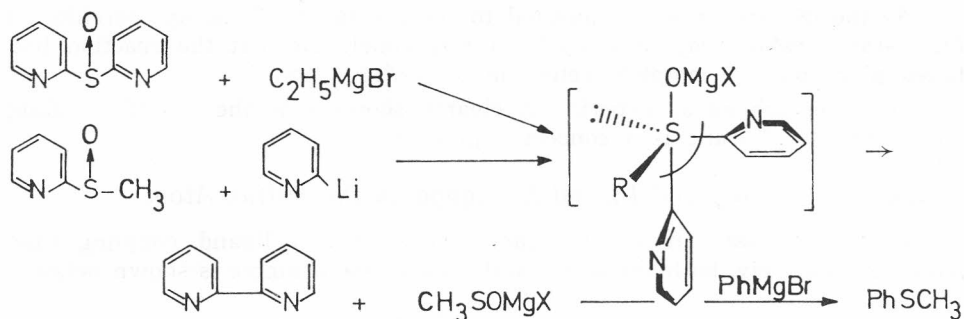


There are also cases in which ligand exchange is the only reaction observed, as in the reaction of aryl alkyl sulfoxides with alkyllithium.²⁵

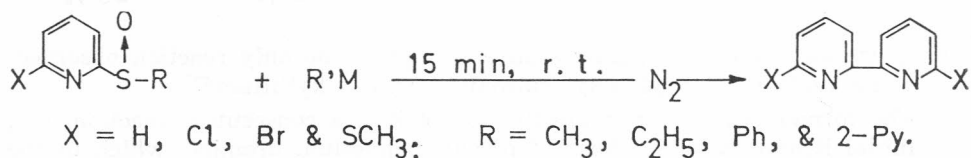
The former reaction is interesting, since it is a consecutive reaction, *i. e.*, the initial ligand exchange forms 2-pyridylmagnesium bromide, which in the subsequent step further reacts with the original sulfoxide to afford eventually 2,2'-dipyridyl, the ligand coupling product. A similar reaction is observed with benzothiazoyl benzyl sulfoxide, as shown above. In this case, however, the ligand exchange reaction was found to compete with the coupling to afford benzothiazole.

The intervention of 2-pyridylmagnesium bromide as the initial intermediate in the reaction of 2-pyridyl methyl sulfoxide with the Grignard reagent may be verified by the following trapping experiment with PhCHO and the two similar reactions, *i. e.*, the one between 2,2'-dipyridyl and ethylmagnesium bromide and the other between 2-pyridyl methyl sulfoxide and 2-pyridyllithium, to afford 2,2'-dipyridyl, as shown below.





Although the yield of 1-phenyl,1-pyridylcarbinol is ca. 15%, while that of phenyl methyl sulfoxide is about 40%, all these reactions clearly reveal that the initial step of the reaction between 2-pyridyl methyl sulfoxide and phenylmagnesium bromide is the ligand exchange forming 2-pyridylmagnesium bromide, which in the subsequent step reacts with the original sulfoxide to afford 2,2'-dipyridyl, the ligand coupling product. This is convenient method of preparing various 6,6'-substituted 2,2'-dipyridyls, as shown below.²⁷

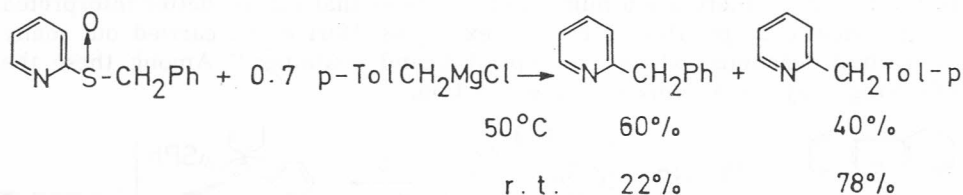
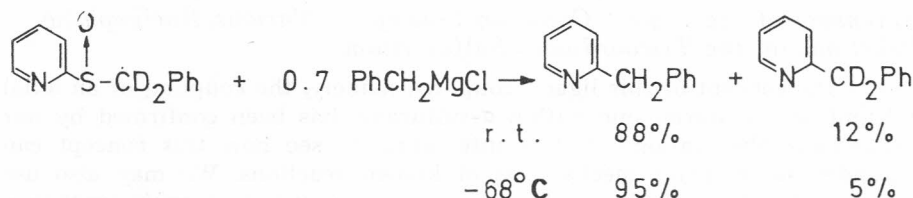


D. Ligand Coupling and Pseudo-rotation

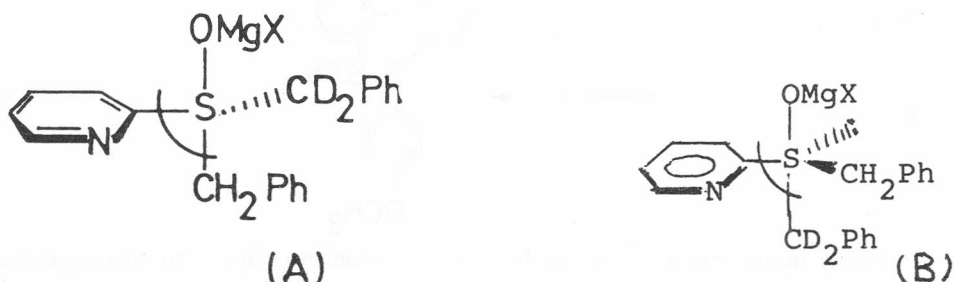
In the reaction of 2-pyridyl benzyl sulfoxide with either alkyl- or arylmagnesium halide or in that of 2-pyridyl alkyl or aryl sulfoxide with benzylmagnesium halide, the ligand coupling always takes place between 2-pyridyl and benzyl groups, as shown previously. This means that, regardless of the incoming nucleophile which approaches the central sulfur atom from an axial direction, pseudo-rotation will put the 2-pyridyl group into an equatorial position and the benzyl group on an axial coordinate for a facile ligand coupling. In the coupling of two 2-pyridyl groups from 2,2'-dipyridyl sulfoxide, pseudo-rotation seems to proceed quite fast to place one 2-pyridyl group into an equatorial and another into an axial position prior to the coupling of the two 2-pyridyl groups.

However, there are cases in which ligand coupling proceeds faster than pseudo-rotation. Such an example is the coupling of two phenyl groups in the reaction between *N-p*-tosyldiphenylsulfilimine and phenylmagnesium bromide, as clearly revealed by our earlier ¹⁴C tracer experiment, described in section A.¹⁹

One of our interesting observations is on the reactions shown below.²⁸ When the reaction was carried out at a low temperature, the incoming benzyl group was found to couple preferentially with the 2-pyridyl group. Since the incoming Grignard reagent is considered to attack the central sulfur atom from an axial direction to form the following incipient sulfurane



intermediate (A), the incoming benzyl group has a better chance to couple with 2-pyridyl group at an equatorial position, whereas the original sulfoxide has to undergo pseudo-rotation to form another intermediate, (B), prior to the coupling between the 2-pyridyl and benzyl-D₂ groups.

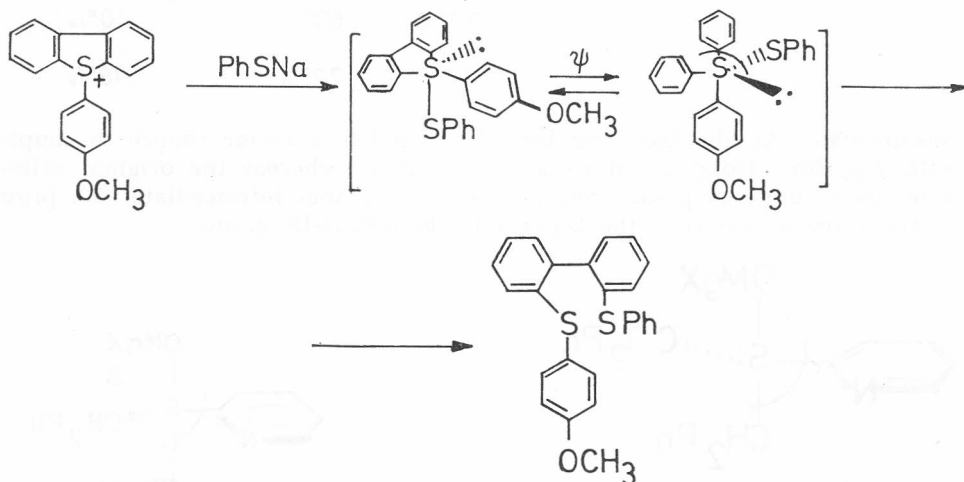


Even at room temperature, ca. 20 °C, ligand coupling seems to proceed faster than pseudo-rotation, which, however, starts competing with ligand coupling. In the latter reaction, the incoming benzylic group no longer preferentially couples with the 2-pyridyl group at a higher reaction temperature, (ca. 50 °C). Thus, in this particular case, the pseudo-rotation seems to become faster, relative to the ligand coupling, as temperature increases. However, until some kinetic measurements are made on both the ligand coupling and pseudo-rotation with various ligands, no general conclusion can be drawn on the structural relationship between ligand coupling, pseudo-rotation and ligand exchange.

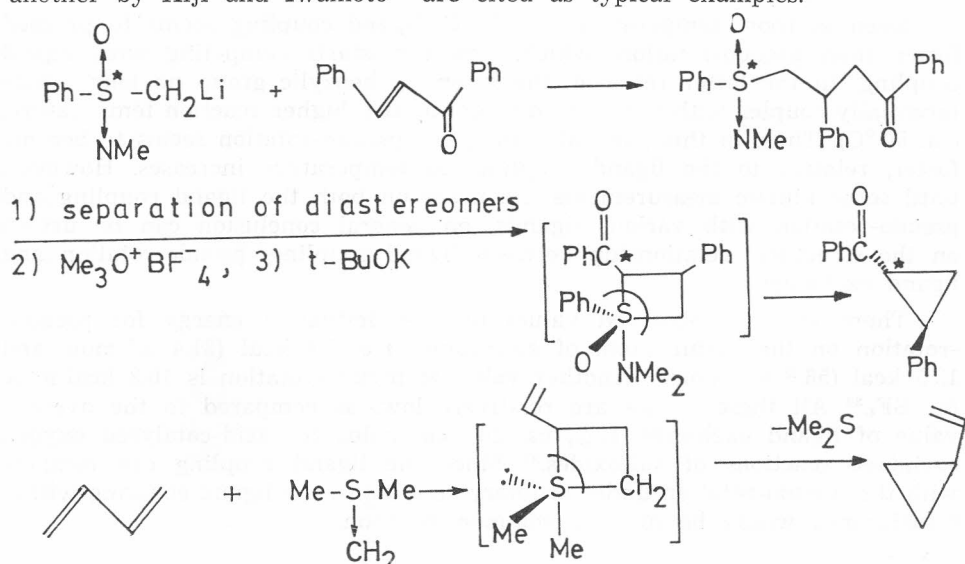
There are two observed values of free activation energy for pseudo-rotation on the sulfur atom of sulfuranes, *i. e.* 7.4 kcal (31.4 kJ/mole and 13.5 kcal (56.6 kJ)/mole.²⁹ Another value of pseudo-rotation is 10.3 kcal/mole for SF₄.³⁰ All these values are relatively low, as compared to the average value of ligand exchange, e. g., ca. 20 kcal/mole., for acid-catalyzed oxygen exchange reactions of sulfoxides.³¹ Since the ligand coupling can compete with the pseudo-rotation under ordinary conditions, the ligand coupling within σ -sulfuranes would be quite a common reaction.

E. Extension of the Ligand Coupling Concept to Various Nucleophilic Reactions on the Tricoordinate Sulfur Atom

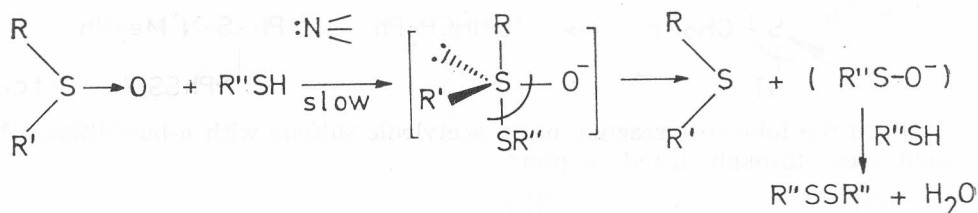
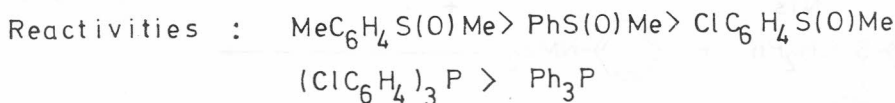
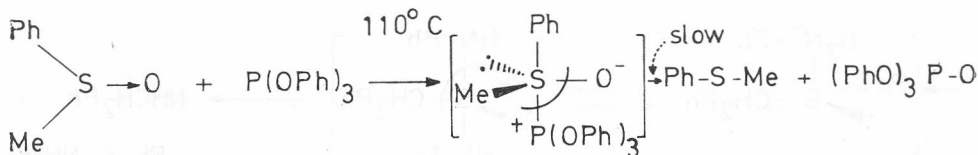
Since the concept of this ligand coupling, namely, the coupling of an axial ligand and an equatorial one within σ -sulfurane, has been confirmed by our stereochemical observation,^{22,23} it is interesting to see how this concept can be extended to interpret mechanisms of known reactions. We may also use this concept for discovering many new reactions, useful for organic syntheses. In the literature there are a number of reactions that can be better interpreted by this new concept. Here are some examples. Hori et al. carried out many interesting reactions, which are typical ligand couplings.³² Among these the following may be a representative reaction.



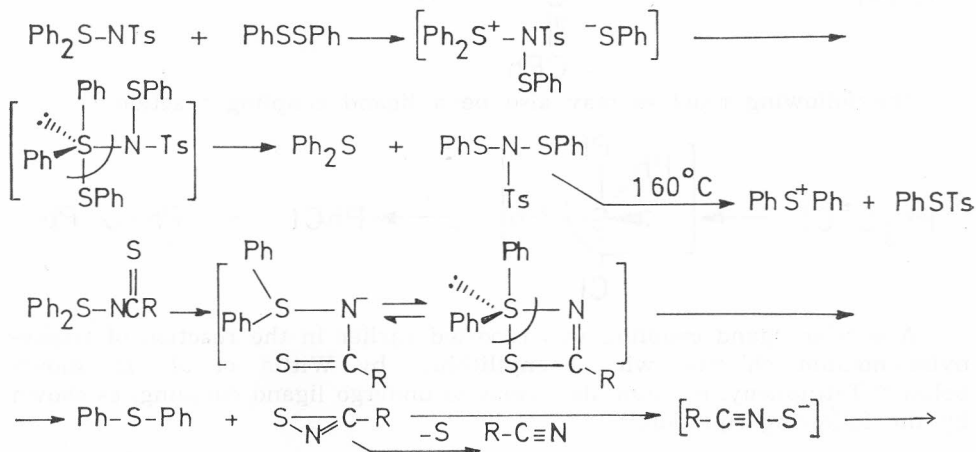
Among many nucleophilic additions of sulfonium ylides to electrophilic conjugate olefins a reaction described by Johnson and his coworkers³³ and another by Kiji and Iwamoto³⁴ are cited as typical examples.



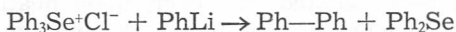
Reduction of sulfoxides by treatment with triphenyl phosphite³⁵ or with thiols in the presence of amines³⁶ may also be a ligand coupling reaction.

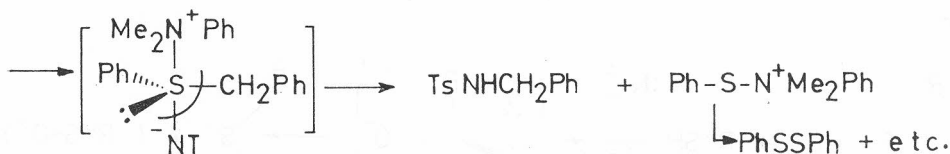
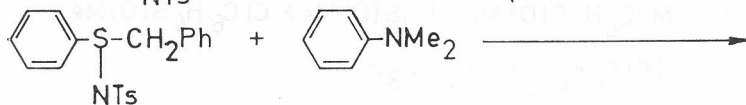
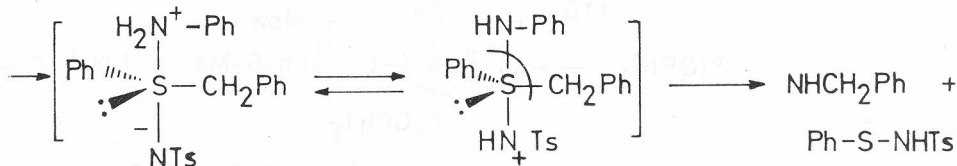
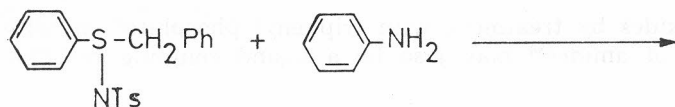


The following two reactions of sulfilimines probably also proceed through ligand coupling.^{37,38}

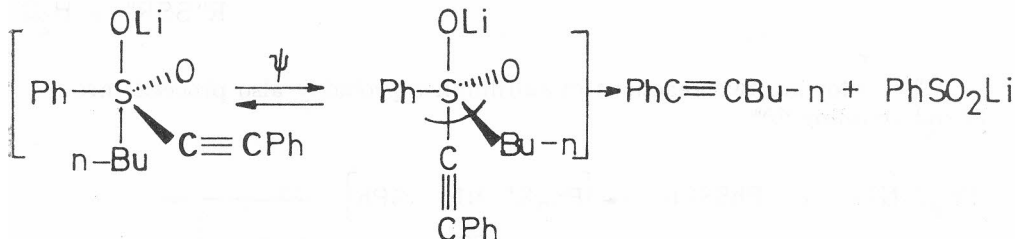


An interesting example are the following two different reactions.³⁹ A stereochemical study of these reactions should prove the occurrence of ligand coupling.

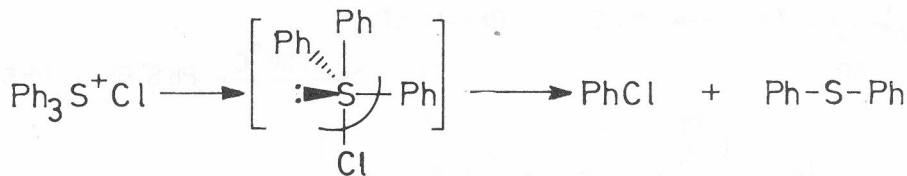




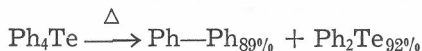
Even the following reaction of an acetylenic sulfone with *n*-butyllithium⁴⁰ could occur through ligand coupling.



The following reaction may also be a ligand coupling reaction.⁴¹



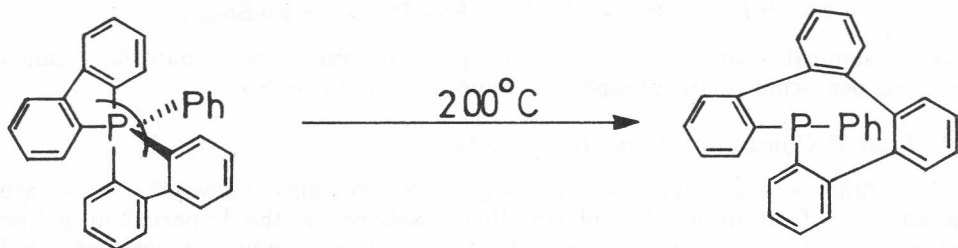
A similar ligand coupling was reported earlier in the reaction of triphenylselenonium chloride with phenyllithium by Wittig et al., as shown below.⁴² Tetraphenyltellurium also seems to undergo ligand coupling, as shown by the following equation.⁴³



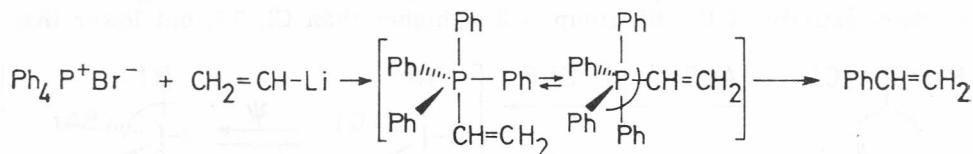
F. Ligand Coupling on the Phosphorus Atom

Pentacoordinate phosphoranes seem to be more stable than σ -sulfuranes and have, therefore, been isolated. However, upon heating at a high temperature, a pentaarylphosphorane was found to undergo ligand coupling, as

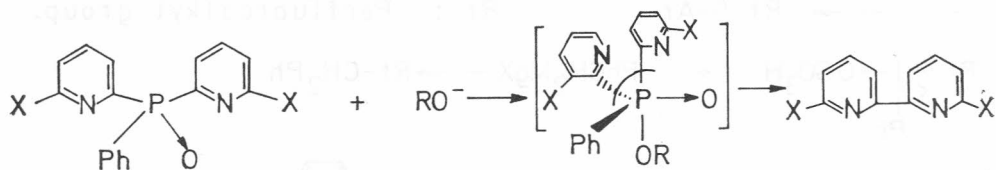
shown below.⁴⁴ A facile ligand coupling reaction is found in the cited



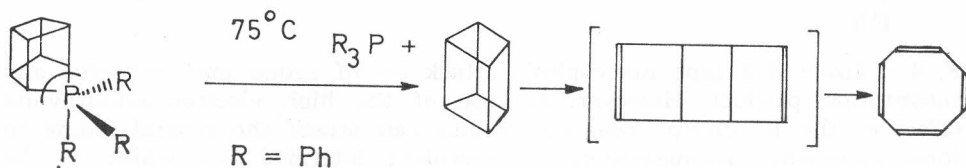
literature, as shown below.⁴⁵



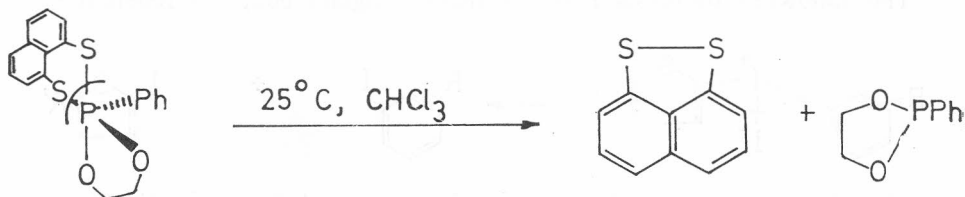
There is a reaction in which two 2-pyridyl groups couple on the pentacoordinate phosphorus atom, as shown below.⁴⁶ The reaction giving



cyclooctatetraene, as shown below,⁴⁷ seems to involve ligand coupling as



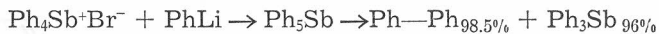
the initial step of the reaction. Another example is the following reaction.⁴⁸



A ligand coupling may be observed in the reported reaction of pentacoordinate arsenic compound presented below.⁴⁹ Tetraphenylantimony bromide also seems to react in the same way to afford the coupling product,



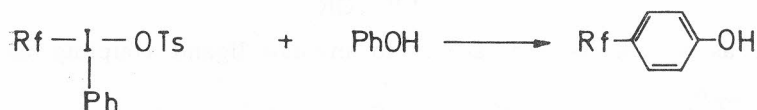
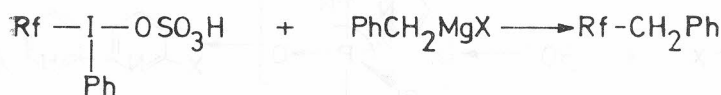
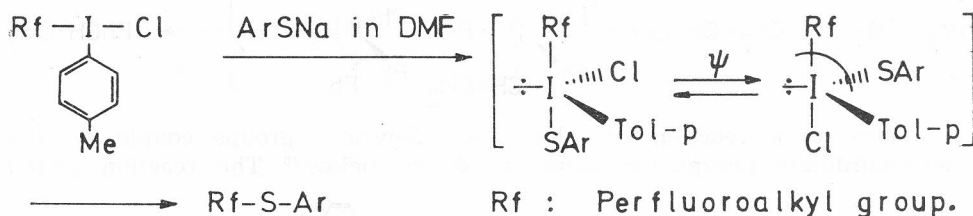
i. e., diphenyl.⁴⁹ Unfortunately, there has been no



stereochemical study to verify the coupling of axial and equatorial ligands on the pentacoordinate phosphorus atom, or on As or Sb.

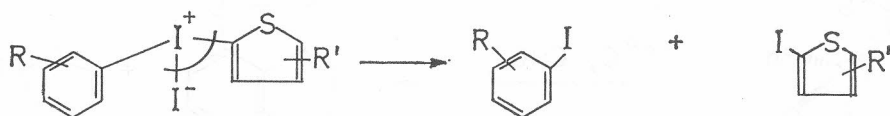
G. Ligand Coupling on the Iodine Atom

Iodine-centered hypervalent compounds are also known.⁵⁰ There are a number of seemingly ligand coupling reactions on the hypervalent iodine atom. An interesting example may be the reaction in which a perfluoroalkyl group couples with a nucleophile, as shown by the following three typical reactions.^{51,52} Since the perfluoroalkyl group is highly electronegative, *i. e.*, electronegativity of the Rf group is 3.45 higher than Cl, 3.0, but lower than

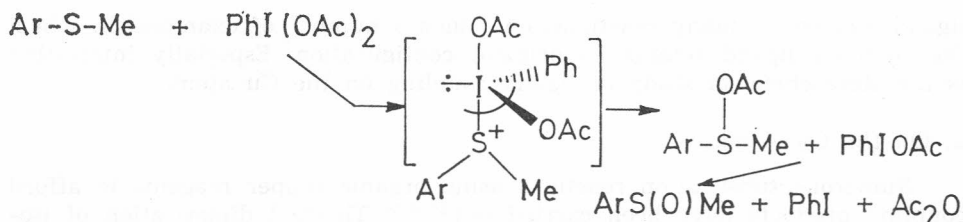


F, 4.0, direct S_N2 type nucleophilic attack on Rf group may not give any substitution product. However, because of the high electron-withdrawing effect of the Rf group, most nucleophiles can attack the central iodine to form incipiently iodine-centered hypervalent intermediates, which in the subsequent step readily undergo ligand coupling. Here again, there has been no stereochemical investigation to substantiate the mechanistic argument.

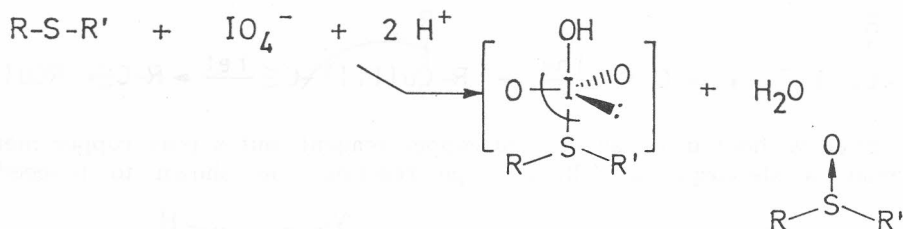
The following pyrolysis may be another ligand coupling reaction.⁵³



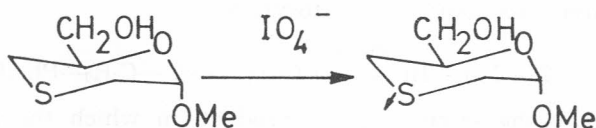
Phenyliodoso diacetate is a good oxidizing agent for converting sulfides to sulfoxides. A kinetic study of the oxidation of substituted phenyl methyl sulfides with this reagent has revealed that the rates correlate nicely with the Hammett σ -values, giving a ρ -value of -0.8 .⁵⁴ This may mean that the reaction is another example of ligand coupling which involves the nucleophilic attack of the sulfide on the central iodine atom, as shown below.



Alkali metal periodates are excellent oxidants of sulfides, which can be converted to the corresponding sulfoxides. The reaction is known to be acid-catalyzed,⁵⁵ and could be another ligand coupling reaction, as shown below.



If the nucleophilic attack of the sulfide on the hypervalent iodine atom is involved in oxidation with periodate, the sulfur atom of the sulfide will attack from the less hindered side. Indeed, in the oxidation of 1,4-oxathiane, shown below, the sulfoxide obtained is a thermodynamically unstable *cis* isomer.⁵⁶



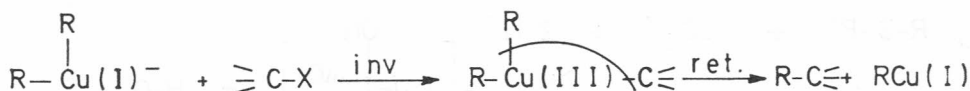
H. Ligand Coupling on Transitional Metal Atoms

Numerous investigations have been carried out on the reactions of organometallic compounds. The uses of transition metal elements, such as copper, palladium, iron and other similar elements, for ligand coupling processes have extended enormously the area of organic syntheses. As the development has been so fast and the amount of research so great, it is impossible to undertake a literature survey which would elucidate the mechanisms of many known reactions. Therefore, this author has no intention of making a thorough rationalization of what has been accumulated on these reactions in the past. However, it would be interesting to see how the concept of ligand coupling on the hypervalent atom may be related to some particular reactions taking place on some metal atoms. If any similar ligand coupling took place on a particular metal atom, one might expect a similar stereochemistry, *i. e.*, retention of the configuration of the coupling

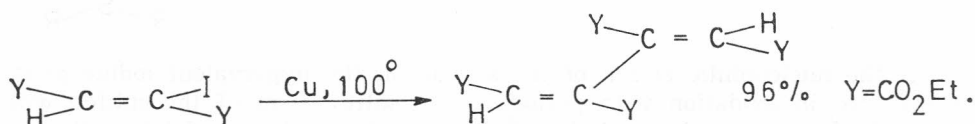
ligand. Indeed, in many reactions, one finds a number of examples in which the coupling ligand retains its original configuration. Especially interesting is the stereochemical study of ligand coupling on the Cu atom.

a. On the Cu Atom

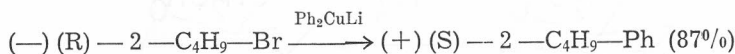
Numerous substitution reactions using organic copper reagents to afford coupling products have been carried out.^{57,58,59} Thermal dimerization of isomerically pure alkenyl copper species with essentially complete configuration retention has been chosen to indicate that the coupling is not a free radical reaction but a concerted, probably an orbital-controlled process after the initial S_N2 type substitution, as shown below,⁶⁰ when Gilman-type cuprates R_2CuLi are used.



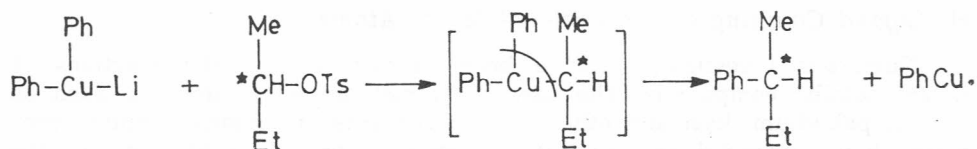
Even without using an organic copper reagent, but a pure copper metal instead, a stereospecific Ullman type reaction was shown to proceed.⁶⁰



In the following reaction of the optically active secondary butyl bromide with Ph_2CuLi , the 2-butyl group in 2-butylbenzene, obtained in an excellent yield, was found to be inverted almost quantitatively.⁶¹ A similar reaction of optically active secondary butyl tosylate



with Ph_2CuLi gave the same coupling product, in which the 2-butyl group was found to be inverted completely.⁶² Thus, the following mechanistic path may be suggested. This could be a kind of a ligand coupling reaction on the



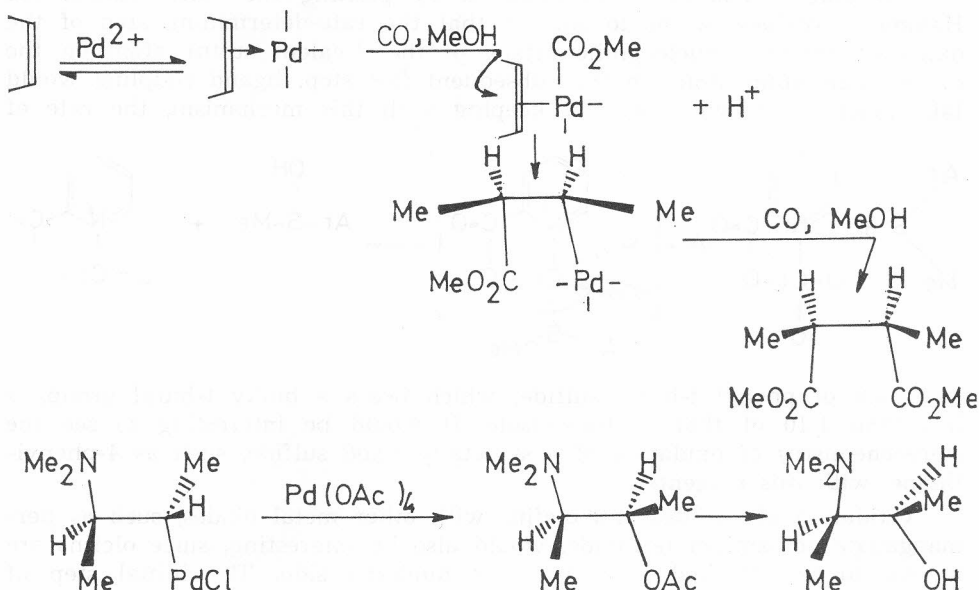
valence-shell expanded copper atom. A similar quantitative inversion of the optically active 2-octyl group in 3-methylnonane, obtained in a fair yield in the reaction of $Et(Me)CuLi$ with optically active 2-bromooctane, was observed.⁵⁹ An intriguing observation relating to stereochemistry is that when $(S)(-)$ -2-iodobutane was treated with Ph_2CuLi , the resulting sec-butylbenzene was found to be nearly completely racemic,⁵⁹ though there is another report which claims that the reaction of lithium dihydroanthracenyl cuprate with $(+)$ -2-iodooctane gave 9-(2-octyl)-9,10-dihydroanthracene, in which the 2-octyl group was found to be 68–70% inverted.⁶⁴ Different

stereochemical behaviour of alkyl iodides in the reactions with organocuprates was suggested to be due to the occurrence of a certain free radical process involving electron transfer. In view of the high reactivity and polarizability of the iodides, along with the facile accommodation of electrons into the valence shell to form the hypervalent iodine intermediates, the initial S_N2 type process for the reaction of alkyl halides with organocuprates may be different with the iodides. Perhaps, some mechanistic studies, including kinetics, are necessary for a better understanding of these interesting reactions.

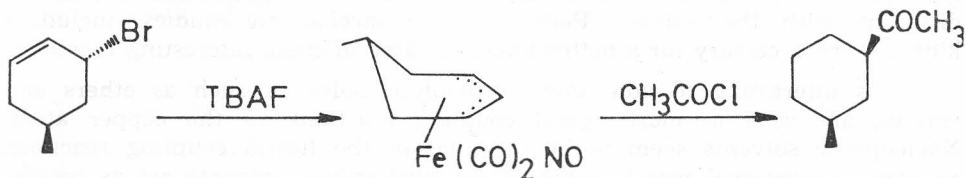
It is interesting to note that nucleophilic solvents, such as ethers and amines, are used in most ligand coupling reactions on the copper atom. Nucleophilic solvents seem to be essential in the ligand coupling reactions on other transitional metal atoms. These nucleophilic solvents act as coordinating ligands to the central metal atom, which in turn becomes so rich with excess electrons that two ligands are readily extruded concertedly from the central atom by coupling. Perhaps, a certain weak interaction, such as that of orbitals, is required for coupling ligands to be placed on nearly perpendicular coordinates.

b. On the Pd and Fe Atoms

Very much work has been done on the use of Pd catalysts for organic syntheses and many useful industrial processes have been developed. However, the mechanistic features of many of these reactions are still not fully understood, mainly due to the difficulties in studying their kinetic behaviour and stereochemistry. It is interesting to note that the coupling of an alkyl ligand and another organic species, e. g., CO, on Pd, seems to proceed with the retention of configuration, as shown by the following two examples.^{65,66} This is only a tiny fraction of the vast amount of work suggesting that the ligand coupling proceeds with configuration retention.



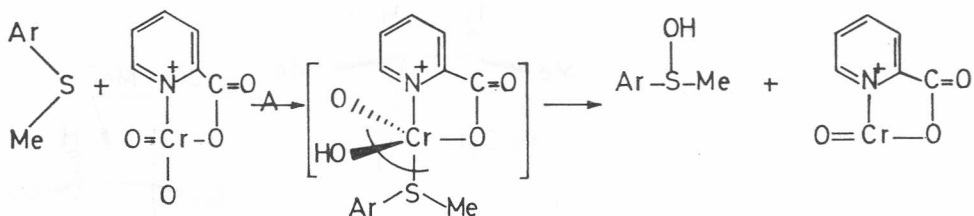
Cobalt carbonyl, $\text{Co}_2(\text{CO})_8$, nickel carbonyl, $\text{Ni}(\text{CO})_4$ and iron pentacarbonyl, $\text{Fe}(\text{CO})_5$, are frequently used for carbonylation of aryl and allylic groups, i. e., coupling of an aryl or allylic ligand with CO. A recent stereochemical study of carbonylation with tetrabutylammonium ferrate, $\text{Bu}_4\text{N}^+ [\text{Fe}(\text{CO})_5\text{NO}]^-$ (TBAF), is shown below.⁶⁷ In this reaction, the first step pro-



ceeds with the inversion of configuration around the cyclohexenyl carbon atom and the second step, i. e., coupling of two ligands, is a retention process, like in the similar carbonylation reaction with Pd catalysts. Although no stereochemical study with optically active alkyl derivatives has been carried out, the stereochemical behaviour would be identical, since the coupling of two ligands on a transition metal atom would take place keeping the angle of the two ligand linkages at about 90° .

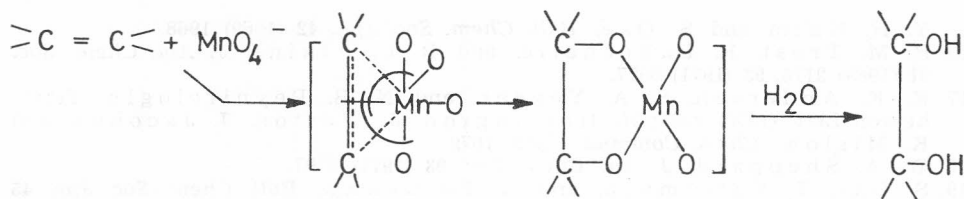
I. Oxidation of Heteroatoms with Metal Oxides

Certain metal oxides such as permanganate, MnO_4^- , and acid chromate, HCrO_4^- , are known to attack oxygen atoms to heteroatoms, and the reaction is usually acid-catalyzed. An interesting example is the following oxidation of aryl methyl sulfides with acid chromate, catalyzed by picolinic acid.⁶⁸ Although the oxidation has been suggested to involve the initial rate-determining one electron transfer (SET) from the sulfur atom to chromate, the high ρ -value, -1.66 at 40°C , obtained by plotting the rates against the Hammett σ -values, seems to suggest that the rate-determining step of the oxidation involves nucleophilic attack of the divalent sulfur atom on the central chromium atom. In the subsequent fast step, ligand coupling would take place as shown below. In keeping with this mechanism, the rate of



oxidation of phenyl *t*-butyl sulfide, which bears a bulky *t*-butyl group, is less than 1/10 of that of thioanisole. It would be interesting to see the stereochemistry of oxidation of a skeletally fixed sulfide, such as 4-phenylthiane, with this reagent.

Oxidation of sulfides and olefins with other metal oxides, such as permanganate or osmium tetroxide, would also be interesting, since olefins are known to be attacked from the less hindered side. The initial step of



these reactions could be the nucleophilic attack of either the divalent sulfur atom or $\text{C}=\text{C}$ double bond on the metal atom, followed by internal ligand coupling, as shown below, though this speculation has to be tested by further experiments.

J. Conclusion

A new concept of ligand coupling within hypervalent intermediates is presented with numerous experimental data to support the argument, especially reactions involving the attack of nucleophiles on the tricoordinate sulfur atom. This new concept has been shown to have the potential of rationalizing many hitherto unexplained coupling reactions and even some oxidation reactions. It would be quite interesting to see how this concept could be used for discovering many new reactions in the future.

Acknowledgement. — Many colleagues have collaborated in pursuing this work. Professors N. Furukawa, Y. H. Kim, Dr. T. Aida and Dr. T. Yoshimura contributed very much to discovering many new interesting reactions on the tri-coordinate sulfur atom in the period when we were at the Osaka City University. In recent years, the earnest efforts of Dr. T. Kawai at the University of Tsukuba are most treasured. Mr. Y. Kotera at U. T. and Mr. T. Takeda at the O.U.S. have also worked with enthusiasms. In the process of shaping up this concept, many old and new friends have offered their kind opinions and criticisms, for which the deepest gratitude is expressed.

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POVZETEK

Vezava ligandov na hipervalentne in podobne intermediate z razširjeno valenčno lupino

Shigeru Oae

Predstavljen je nov koncept vezave ligandov v hipervalentnih intermediatih. Številni eksperimentalni podatki podpirajo to trditev, še posebej reakcije, pri katerih pride do napada nukleofilov na trikoordinatni žveplov atom. Po tem konceptu je mogoče razložiti številne dosedaj nepojasnene reakcije vezave in celo nekatere procese oksidacije.