

in targets by the impact process. With metal targets, craters containing evidence of jet formation were observed. Studies with larger, more energetic clusters may shed some light on this point.

So far the phenomenon of cluster fusion has been confirmed in one other laboratory.¹¹ The experimental evidence tends to support the conclusion that dynamic energy focusing that generates high-velocity deuterons can occur in cluster impacts on solids. In another study¹² an attempt was made to produce D-D fusion with D₂ clusters impacting on deuterated surfaces. No fusions were observed. These results can be interpreted as evidence for the need for heavier atoms to establish an energy amplification mechanism. The Lyon group¹² used beam intensities an order of magnitude smaller than ours and did not establish the integrity of the cluster beam at the target with secondary electron analysis. The failure to use beam diagnostics at the target and the sensitivity of cluster fusion reactions to possible target contamination not completely removed in experiments with low beam intensities could possibly account for failure to observe fusion reactions. In our experiments the observation of cluster fusion events depended on maintaining beam intensities above some critical level that would minimize contamination of the target surface. With beams of more than about 0.5 nA, the fusion yields scaled linearly with beam intensity.

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At lower beam intensities, fusion yields decreased faster than beam currents when the current was varied. Our studies with targets coated with thin gold films⁶ also revealed a very high degree of sensitivity of cluster fusion reactions to target surface contamination.

The results obtained in cluster fusion studies are remarkable in that they suggest that the collective interaction of atoms in large molecular projectiles with target atoms can generate "unexpected" energy distributions. The observation of fusion events has so far not been explained by model calculations. Models employing a "Fermi shuttle" in which a pair of deuterons is compressed between a pair of heavy atoms have been proposed.¹³⁻¹⁵ This model provides for some energy amplification in a fraction of the hot atoms generated by the cluster impact. Little or no evidence could be found for significant energy amplification with computer simulations that were based on two-body interactions.⁸ But so far computer simulations with acceleration of light particles by repeated scattering between heavy beam particles still fail to explain the experimental results. The original discrepancies, as large as 80 orders of magnitude with larger clusters, are reduced to discrepancies ranging from 8 to 18 orders of magnitude. We conclude that the experiments have uncovered an energy amplification mechanism that is operative on a microscopic scale and that is possibly similar to energy-amplification mechanisms observed with macroscopic shaped-charge phenomena.

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Ligand-Coupling Reactions of Hypervalent Species

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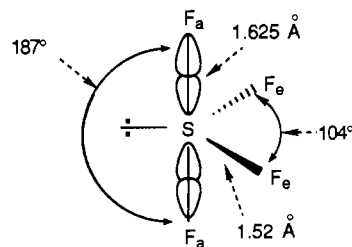
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A typical example of a three-center, four-electron bond, called a hypervalent bond by Musher,¹ can be found in the structure of SF₄, as demonstrated by X-ray crystallographic analysis by Rundle et al.² and Pimentel.³ The central atom in a hypervalent species is va-

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lence-shell-expanded and tends to extrude one pair of electrons to assume the normal valency of an octet. There are three conceivable ways for hypervalent

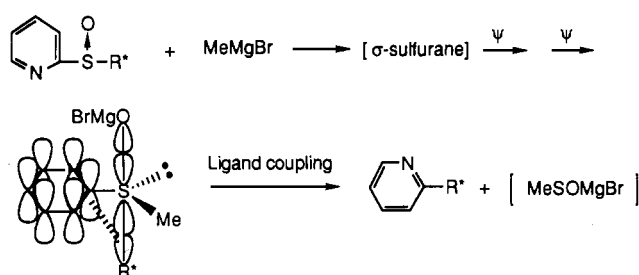
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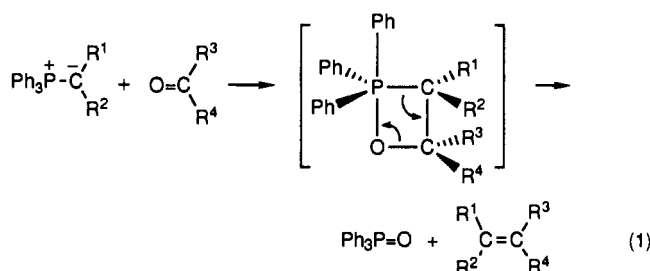
(3) Pimentel, G. C. *J. Chem. Phys.* 1951, 19, 446.

Scheme I

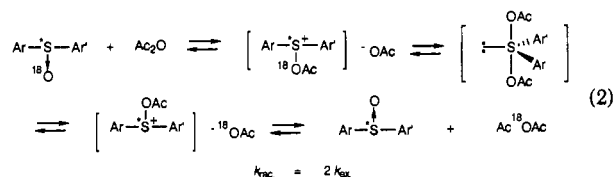


species to collapse to form stable species: *self-decomposition* as exemplified by the well-studied Wittig reaction,⁴ *ligand exchange*,^{5,6} and *ligand coupling*.⁷⁻¹¹

One example of *self-decomposition* is the Wittig reaction shown by eq 1. The formation of an oxaphosphetane as an intermediate is beyond any doubt. In this case, the high energy gained by formation of the P=O bond, ca. 536–678 kJ, would outweigh other possible reactions.



Ligand exchange is the best known reaction of hypervalent species and proceeds either through a typical $\text{S}_{\text{N}}2$ -type stereochemical path involving an intermediate, as illustrated by the oxygen exchange shown in eq 2, or through an intermediate that undergoes pseudorotation prior to elimination of the leaving group, eventually affording a product that retains its configuration (eq 3).^{12,13}



Ligand coupling is the subject of this Account (Scheme I).

In hypervalent species, electronegative ligands tend to occupy axial positions using p orbitals, while π - or

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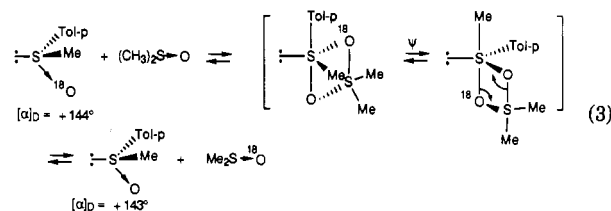
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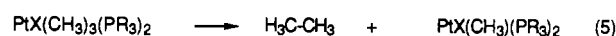
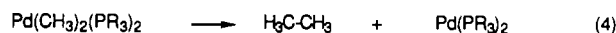


electron-donating ligands favor equatorial positions. The stability of the hypervalent species has some effect on the ease of ligand coupling, but the electronic nature of the central atom appears to be most important. Ligand coupling is a concerted reaction by orbital interaction between an axial and an equatorial ligand, and hence the ligands involved in coupling retain their original configuration. Meanwhile, the ease of ligand exchange, ligand coupling, and pseudorotation, which has to be considered in the hypervalent species, varies, depending upon the central atom and the attached ligands,⁹ although the leaving ability of an exchanging ligand seems to be related to its apicophilicity.⁶ A hypervalent intermediate is formed by the attack of a nucleophile on the central atom of a stable octet, usually at the rate-determining step. The subsequent ligand coupling within the hypervalent intermediate is illustrated in Scheme I for our first stereochemical experiment involving an optically active alkyl 2-pyridyl species and a Grignard reagent.¹⁴

Ligand coupling is considered to take place between the equatorial 2-pyridyl group and an optically active axial R^* group. This configuration may be attained by pseudorotations from the initial form of the σ -sulfurane intermediates formed by the nucleophilic attack of the methyl group on the central sulfur atom along an axial axis. If there is any cohesive interaction between the coupling ligands, they would be concertedly expelled from the central valence-shell-expanded atom, affording a ligand-coupling product in which both ligands would retain their original configuration. In most cases, the cohesive interaction would result from the overlapping of orbitals of both ligands, shown in Scheme I.¹⁵ In this reaction, however, 2-pyridyl is an achiral group, while the R^* group is optically active. Hence, the R^* group in the coupling product should completely retain the optical activity.

NMR spectroscopic observations of the formation of σ -sulfuranes, selenanes, and telluranes prior to ligand coupling have been made earlier by Sheppard¹⁶ and recently by Ogawa.¹⁷

The term “reductive elimination” has been preferentially used to describe the elimination of ligands with concomitant reduction of the valence number of the central metal as exemplified by the reactions shown in eqs 4 and 5.¹⁸⁻²⁴



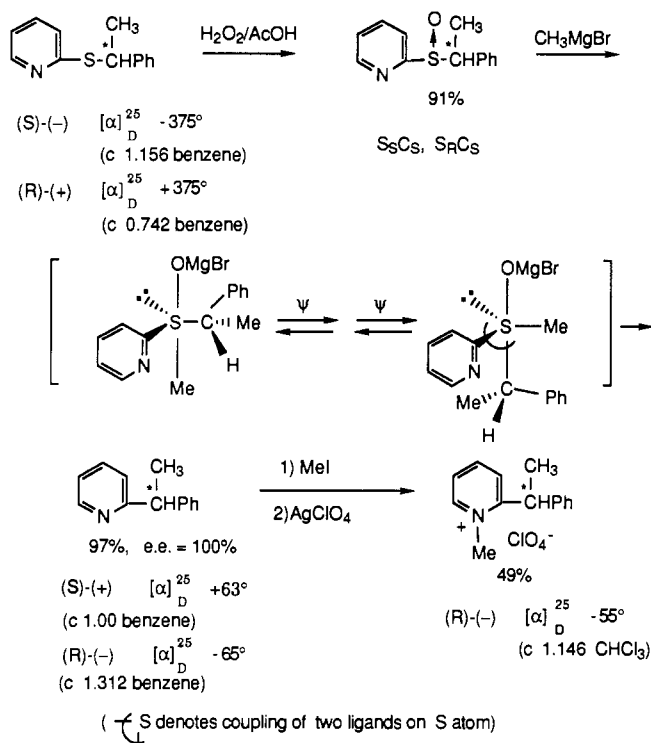
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(15) If the cohesive interaction due to the overlap of p orbitals would be more than a few kilocalories/mole, ligand coupling would proceed readily, since none of these three processes, i.e., ligand coupling, ligand exchange, and topological transformation, would require any more than a few kilocalories/mole of activation enthalpies.

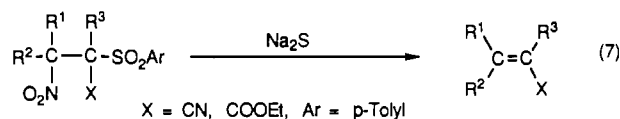
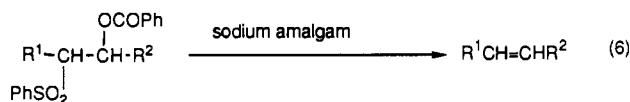
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Scheme II



The expression "reductive elimination" is confusing. In nonorganometallic chemistry, reductive elimination has been used quite often in the synthesis of olefins, as shown by eqs 6 and 7.^{25,26}

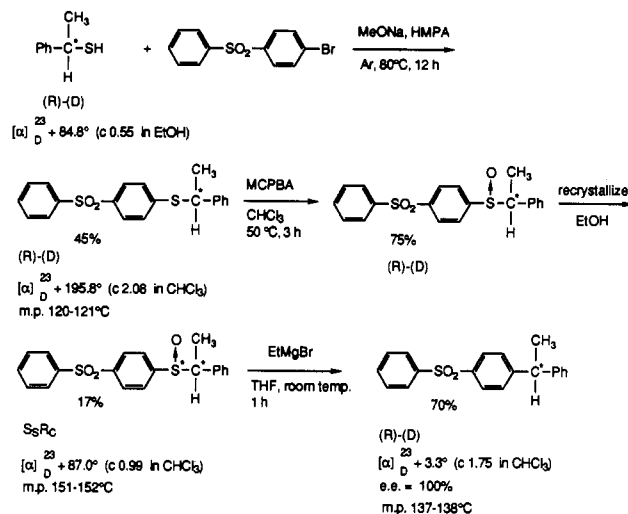


The term "oxidative addition" is used as frequently as "reductive elimination" in organometallic chemistry. This term is also a mere description of the phenomenon and lacks mechanistic significance. However, our concept of ligand coupling has a mechanistic implication, as described above.

Central Sulfur Atom

The first example of ligand coupling within an intermediary σ -sulfurane, which upon collapsing afforded the product in which the stereochemistry around the sp^3 carbon was found to be completely retained, is the

Scheme III



reaction between optically active 1-phenylethyl 2-pyridyl sulfoxide and methylmagnesium bromide. The ligand-coupling product was a liquid, which was converted to the solid *N*-methylated derivative for an X-ray crystallographic analysis. The mechanistic path is shown in Scheme II.¹⁴

In order to avoid the possible chelation of the magnesium atom in the Grignard reagent with the nitrogen atom and the sulfinyl oxygen atom, a stereochemical experiment with optically active 1-phenylethyl *p*-(phenylsulfonyl)phenyl sulfoxide and ethylmagnesium bromide was carried out.²⁷ The result is shown in Scheme III. Here again, the configuration of the 1-phenylethyl group in the resulting 4-(1-phenylethyl)-1-(phenylsulfonyl)benzene was found by X-ray crystallographic analysis to be retained completely.

The concerted nature of the ligand coupling has also been demonstrated by us in the reaction of *p*-(phenylsulfonyl)phenyl crotyl sulfoxide with Grignard reagents to afford 4-(phenylsulfonyl)-1-crotylbenzene, in which the geometric configuration of the crotyl group was completely preserved (eq 8). No rearrangement was observed in the coupling reaction of *p*-(phenylsulfonyl)phenyl α -methylallyl sulfoxide (eq 9). Similarly, complete retention of geometric configurations has been observed in the reactions of *p*-(phenylsulfonyl)phenyl styryl and 2-pyridyl styryl sulfoxides with Grignard reagents (eqs 10-12).²⁸

2-(1-Phenylethyl)quinoline, obtained in the reaction of optically active (*R*)-(+)-phenylethyl 2-quinolyl sulfoxide with a Grignard reagent, has also been shown to completely retain the configuration of the 1-phenylethyl group.²⁹ All of these observations seem to support the concept that ligand coupling is concerted between an axial and an equatorial ligand within a σ -sulfurane intermediate. Thus, the stereochemical outcome alone can often serve as a diagnostic tool as to whether or not the reaction involves ligand coupling.

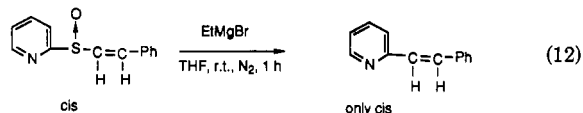
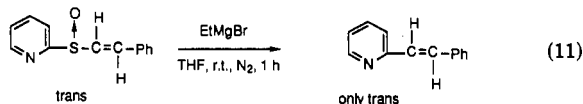
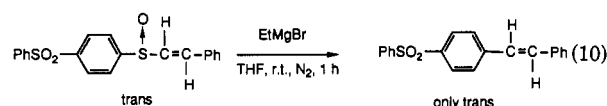
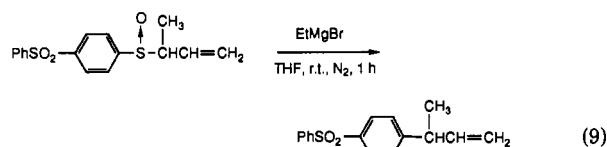
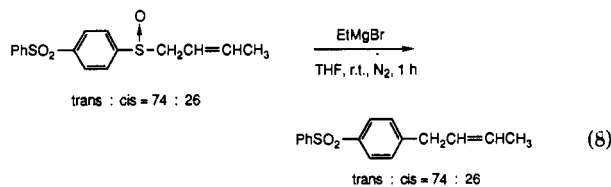
There are cases in which the initial step is ligand exchange and the subsequent fast step is ligand coupling.³⁰ A typical example may be found in the reaction

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 (23) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457.
 (24) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1974**, *65*, 275.
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of an alkyl 2-pyridyl sulfoxide with Grignard reagents, which is a convenient method of preparing 2,2'-bipyridyls and 2,2'-biquinolyls, as shown in Scheme IV. In this reaction, the initial formation of 2-pyridylmagnesium halide was verified by its being trapped with benzaldehyde, affording phenyl-2-pyridylmethanol.

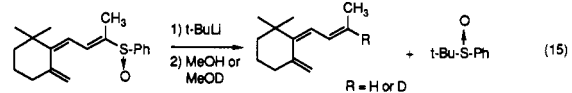
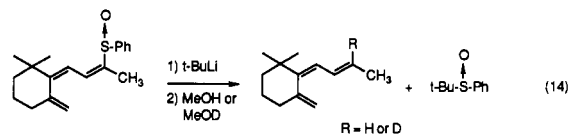
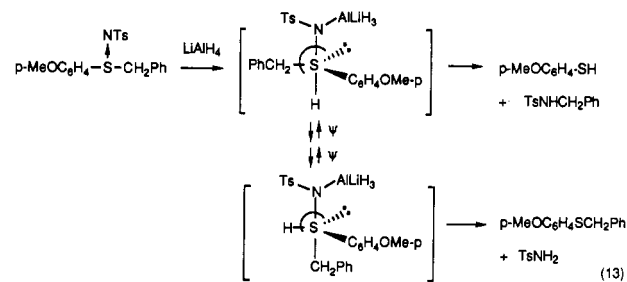
This type of consecutive ligand exchange and coupling is useful in the preparation of oligopyridyls, as shown in Scheme V.³¹

Ligand coupling can be found in the reduction of a sulfilimine with LiAlH_4 (eq 13),³² and ligand exchange is observed in the stereospecific reductive desulfurization of vinyl sulfoxides with *tert*-butyllithium and an internal proton source,³³ as shown by eqs 14 and 15.

Many similar reactions can also be observed, and the overall yields are usually excellent.³⁴ Therefore, those processes are quite useful for organic syntheses. Although this new concept of ligand coupling within the σ -sulfurane has been introduced on the basis of observed reactions of organic sulfur compounds, it is universal for understanding the general nature of the reactions of hypervalent species in which the central atoms are other than sulfur.

Central Phosphorus Atom

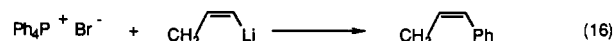
Phosphine oxides bearing two or three 2-pyridyl groups have also been found to react with organo-



metallic reagents, affording 2,2'-bipyridyl, substituted pyridines, and pyridine in good yields.³⁵ Here again, both independent ligand exchange and ligand coupling as well as consecutive ligand exchange and coupling can be observed (Scheme VI).

Phosphonium salts bearing at least two 2-pyridyl groups behave similarly. These phosphorus compounds gave the corresponding 2,2'-bipyridyls and pyridines in substantial yields upon treatment with acid or even with neutral solvents such as water or alcohols.³⁶ All these reactions are ligand couplings within the penta-coordinated phosphorus intermediates formed transiently during the reactions.³⁵ While the reaction of the phosphorus compounds with organometallic reagents would be the same as the reaction of the organosulfur species, the ligand-coupling reaction in the acidic media is considered to proceed through the path shown in Scheme VII.³⁷

Although no reaction has been performed with optically active alkyl-substituted phosphine oxides or phosphonium salts, the reactions of tetraphenylphosphonium bromide with *cis*- and *trans*-propenyllithiums were reported to afford propenylbenzene with nearly exclusive retention of geometric configuration of the propenyl groups,³⁸ shown by eqs 16 and 17.



A preliminary MO calculation suggests that the penta-coordinated phosphorane is more stable than the corresponding σ -sulfurane.³⁹ There are many known examples of ligand coupling within the pentacoordinate phosphoranes. Many of these phosphoranes are short-lived intermediates, but some have been isolated.^{5,6}

The early work of Hey and Ingold,⁴⁰ who claimed to have obtained mixed hydrocarbons by coupling of an

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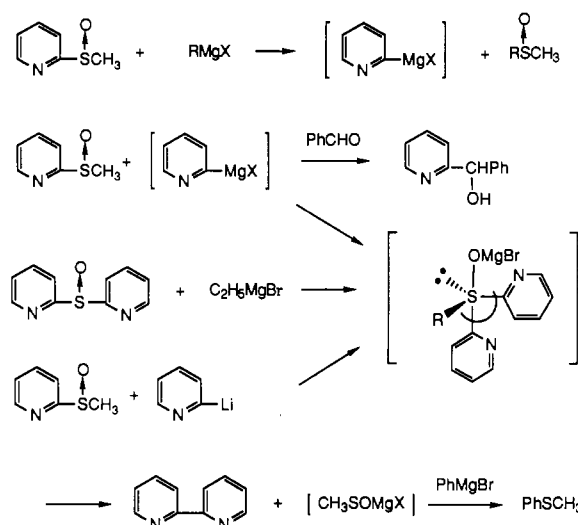
(39) Uchida, Y.; Onoue, K.; Tada, N.; Nagao, F.; Kozawa, H.; Oae, S. *Heteroat. Chem.* 1990, 1, 295.

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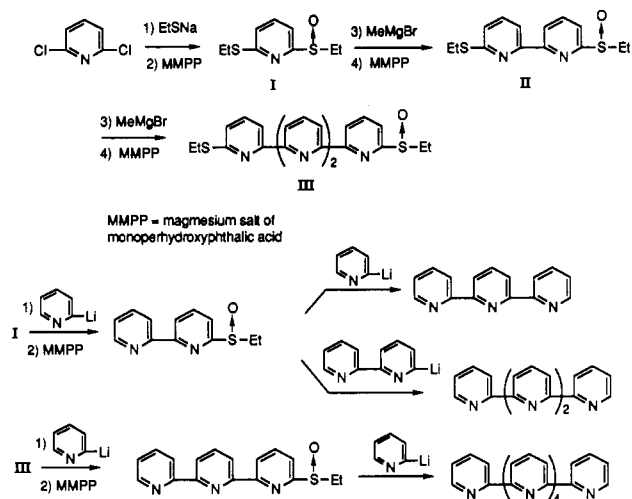
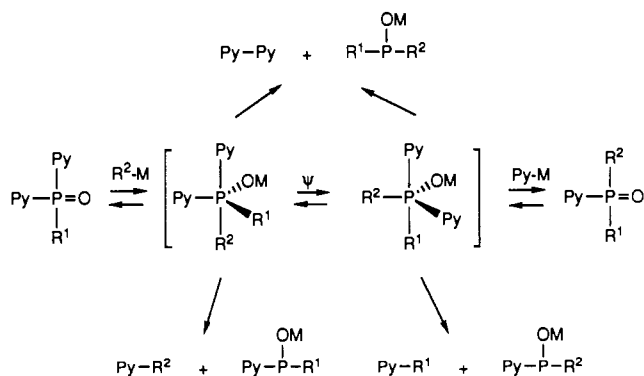
(41) Aida, M., private communication.

(42) Hey, L.; Ingold, C. K. *J. Chem. Soc.* 1933, 531.

Scheme IV



Scheme V

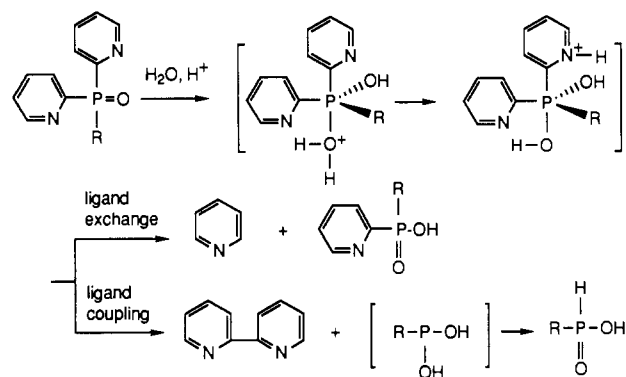
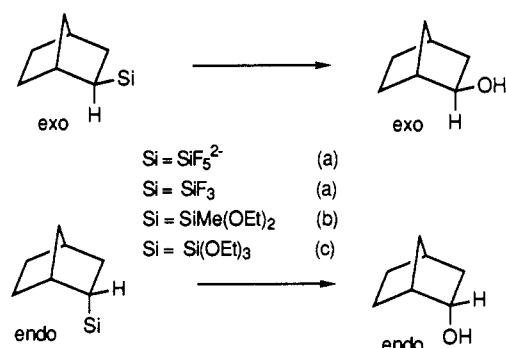
Scheme VI^a

^aPy = 2-pyridyl; R¹ = 2-pyridyl, Ph; R² = Me, Ph, PhCH_2 , 4- $\text{MeC}_6\text{H}_4\text{CH}_2$; M = Li, MgX .

alkyl group on a phosphorus atom with another alkyl group of an alkoxide in the treatment of tetraalkylphosphonium salts with alkoxides, was recently found to be wrong. The reactions of quaternary phosphonium salts with alkoxides were found to involve both ligand exchange and ligand coupling, depending upon the substituents on the phosphorus atom.⁴¹

(41) Uchida, Y.; Oae, S., unpublished.

Scheme VII

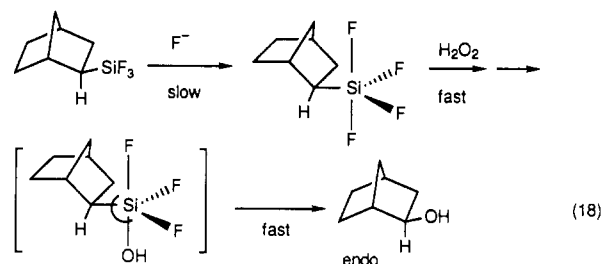
Scheme VIII^a

^aReaction conditions: (a) MCPBA/DMF/room temperature; (b) 30% $\text{H}_2\text{O}_2/\text{KHF}_2/\text{DMF}/60^\circ\text{C}$; (c) 30% $\text{H}_2\text{O}_2/\text{NaHCO}_3/\text{MeOH}/\text{THF}/60^\circ\text{C}$.

Central Silicon Atom

Among numerous reactions involving penta-coordinated silicon compounds,⁷ two typical reactions affording ligand-coupling products that retained the original configurations are shown in Scheme VIII.⁴²

Here again, the rate-determining step seems to be nucleophilic attack,⁴³ namely, the attack of F^- to form a pentacoordinated silicon intermediate. The subsequent fast ligand coupling shown by eq 18 will give alcohols with retention of their configurations. Thus, ligand coupling in the pentacoordinated silicon intermediate is another concerted process.



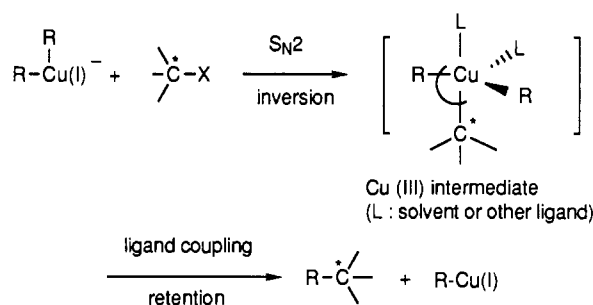
Central Iodine Atom

Iodine-centered hypervalent compounds also are known.⁸ There are a number of apparent 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

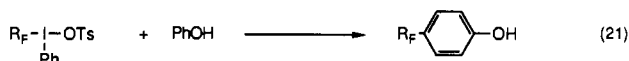
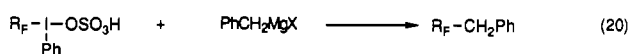
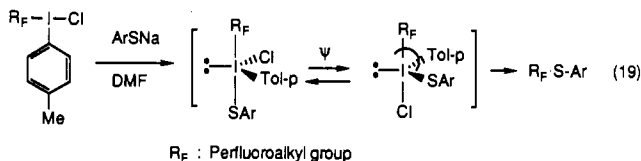
(42) Tamao, K.; Hayashi, T.; Ito, Y. *Nippon Kagaku Kaishi* 1990, 509. Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* 1983, 2, 1694. Tamao, K.; Yao, H.; Tsumami, Y.; Abe, H.; Hayashi, T.; Ito, Y. *Tetrahedron Lett.* 1990, 31, 2925.

(43) Tamao, K.; Hayashi, T.; Ito, Y., unpublished, cited in ref 28.

Scheme IX

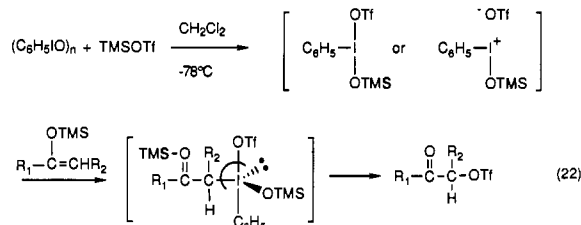


shown by the three typical reactions shown in eqs 19–21.⁴⁴ Since the perfluoroalkyl group is highly



electronegative [i.e., the electronegativity of the R_F group is 3.45,⁴⁵ between that of Cl (3.0) and F (4.0)], a direct S_N2 -type nucleophilic attack on the R_F group may not give any substitution product. However, because of the highly electron withdrawing effect of the R_F group, most nucleophiles can attack the central iodine atom to form transient iodine-centered hypervalent intermediates, which in a subsequent step readily undergo ligand coupling. Here again, there has been no stereochemical investigation to substantiate the mechanistic argument.

The reaction shown in eq 22 to form α -(trifluoromethyl)sulfonyl ketones (α -keto triflates) is another typical example of ligand coupling.⁴⁶



The substitution reactions shown in eqs 23 and 24 were found to be stereospecific and proceeded with retention of the trans configuration of the double bond. Ochiai proposed a reaction pathway involving the initial addition of the cuprate, ligand coupling on the iodine atom, and also ligand coupling on the copper.⁴⁷

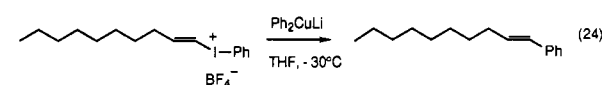
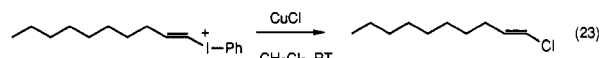
Among many other examples, the oxidation of substituted thioanisoles with (diacetoxyiodo)benzene may

(44) Lyalim, V. V.; Orda, V. V.; Alekseeva, L. A.; Yagupolskii, L. M. *Zh. Org. Khim.* 1971, 7, 1473. Yagupolskii, L. M.; Maletina, I. I.; Kondratenko, N. V.; Orda, V. V. *Synthesis* 1978, 835. Umemoto, T. *Yuki Gosei Kagaku Kyokaiishi* 1983, 41, 251. Umemoto, T.; Kuriu, Y. *Tetrahedron Lett.* 1981, 22, 5197. Umemoto, T.; Miyano, O. *Bull. Chem. Soc. Jpn.* 1984, 57, 3361.

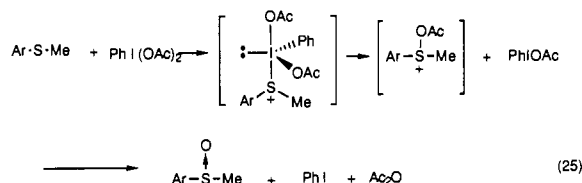
(45) Huheey, J. E. *J. Phys. Chem.* 1965, 69, 3284.

(46) Moriarty, R. M.; Epa, W. R.; Penmasta, R.; Awasthi, A. K. *Tetrahedron Lett.* 1989, 30, 663.

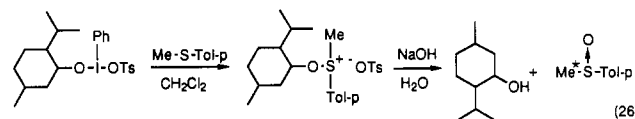
(47) Ochiai, M. *Reviews on Heteroatom Chemistry*; MYU: Tokyo, 1989; Vol. 2, pp 92–112.



be cited (eq 25). In this reaction, the rates were found to be correlated with the Hammett σ values, giving a ρ value of -0.8 ,^{8,48} the rate being slower with bulky alkyl-substituted phenyl sulfides.

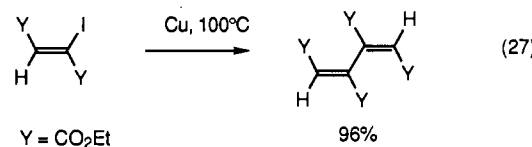


Recently, the reaction shown in eq 26 was found to give methyl *p*-tolyl sulfoxide in nearly optically pure form, due to the optically active nature of the starting material.⁴⁹ This also involves a typical ligand coupling, with initial nucleophilic attack of the sulfide on the hypervalent iodine atom.



Central Copper Atom

As was suggested earlier,^{8,11} many reactions involving organic copper reagents, such as the Ullman type reactions⁵⁰ and those involving the Gilman reagent,⁸ may proceed through ligand coupling. These reactions are highly stereoselective. A typical example of the Ullman type reaction was carried out by Cohen and Poeth, who showed the reaction to proceed with over 96% retention of the geometric configuration, as shown in eq 27.⁵⁰



One example of the use of a Gilman reagent is the formation of optically active 2-phenyloctane in the treatment of optically active 2-octyl *p*-tosylate with lithium diphenylcuprate,⁵¹ though octyl bromide behaved somewhat differently.⁵² Many similar reactions have been carried out with Gilman reagents,⁵³ and all have been found to be stereoselective. The reaction obviously involves an initial S_N2 process,⁵⁴ and the

(48) Srinivasan, C.; Chellamani, A.; Kuthalingam, P. *J. Org. Chem.* 1982, 47, 428.

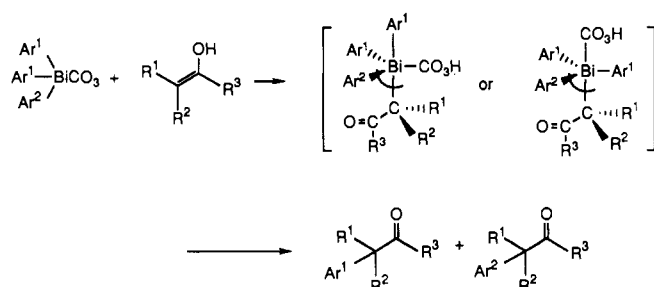
(49) Ray, D. G., III; Koser, G. F. *J. Am. Chem. Soc.* 1990, 112, 5672.

(50) Cohen, T.; Poeth, T. *J. Am. Chem. Soc.* 1972, 94, 4363.

(51) Dagurige, Y. M.Sc. Thesis, Okayama University of Science, 1988.

(52) Lipshutz, B. H.; Wilhelm, R. S. *J. Am. Chem. Soc.* 1982, 104, 4696. Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *The Chemistry of Higher Order Organocuprates*, Tetrahedron Report, No. 176. *Tetrahedron* 1984, 40, 5005.

(53) Posner, G. H. *Substitution Reaction using Organocopper Reagents; Organic Reactions*, 22; John Wiley & Sons: New York, London, Sydney, and Toronto, 1975; pp 252–400. Posner, G. H. *Conjugative Addition Reactions of Organocopper Reagents; Organic Reactions*, 19; John Wiley & Sons: New York, London, Sydney, and Toronto, 1972; pp 1–114. Johnson, C. R.; Dutra, G. A. *J. Am. Chem. Soc.* 1973, 95, 7783. Johnson, C. R.; Dutra, G. A. *J. Am. Chem. Soc.* 1973, 95, 7777. Hebert, E. *Tetrahedron Lett.* 1982, 23, 415.

Scheme X^a

^a $\text{Ar}^1, \text{Ar}^2 = 4\text{-NO}_2\text{C}_6\text{H}_4, \text{CH}_3\text{O}-4\text{-C}_6\text{H}_4, \text{CH}_3-4\text{-C}_6\text{H}_4, \text{Ph}$. Relative migratory aptitude: NO_2 (3.55) > H (1) > CH_3 (0.5) > CH_3O (0.25).

subsequent fast ligand coupling takes place on the hypervalent copper atom (Scheme IX).

Other Central Metal Atoms

Reactions on Ni are quite similar to those on Cu,⁵⁵ as Luh has suggested. Many other reactions on transition metals, such as Fe, Co, Cr, and Pd, proceed similarly, and extremely high stereoselectivities have often been observed.⁸ Many similar reactions can also be found with hypervalent species of other elements, i.e., Se, Te, Bi, Sb, Sn, and others.⁸

Among these, the work of Barton et al.⁵⁶ is shown in Scheme X. Although there is no stereochemical evidence, the relative migratory aptitudes seem clearly to indicate that the *p*-nitrophenyl group, which stabilizes the hypervalent intermediate, tends to undergo ligand coupling more readily.

Another example of a typical ligand coupling is the chromium oxidation of a sulfide (eq 28).⁵⁷ The rate of oxidation of phenyl *tert*-butyl sulfide is less than 1/10 of that of thioanisole, clearly indicating the slow step to be the nucleophilic attack of the sulfide sulfur on the hypervalent Cr atom.

Summary

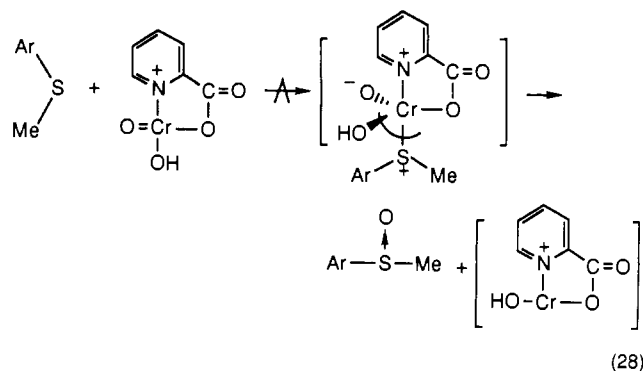
The basic concept of ligand coupling within hypervalent species has been introduced. In nearly all cases,

(54) Whitesides, G. M.; Filippo, J. S.; Stredronsky, E. R.; Casey, C. P. *J. Am. Chem. Soc.* 1969, 91, 6542.

(55) Luh, T.-Y.; Ni, Z.-J. *Synthesis* 1989, 89.

(56) Barton, D. H. R.; Finet, J.-P. *Pure Appl. Chem.* 1987, 59, 936.

(57) Rajagopal, S. Ph.D. Thesis, M. Kumaraj University, 1984.



(28)

retention of configuration of coupling ligands has been observed. This indicates a mechanism involving the concerted front-side coupling between an axial and an equatorial ligand. The stereochemical nature of the reaction has been used to diagnose the occurrence of ligand coupling, whenever there are some stereochemical data available.

If the central atom of the reacting molecule is below the second row of the periodic table and can expand the valence-shell beyond an octet to form a hypervalent species, there is a possibility for ligand coupling to occur within this species.

In organometallic chemistry, the terms "reductive elimination" and "oxidative addition" have been used to describe many chemical phenomena. As has been described elsewhere,¹¹ most of these reactions can be understood in terms of ligand coupling within hypervalent species. Therefore, there are very many reactions that can be interpreted as ligand-coupling processes.^{8,10} Only a few well-defined cases have been chosen for illustration in this Account.

Synthetic applications of ligand coupling are numerous. A few examples have been cited. Since ligand coupling is stereospecific in most cases, the reaction can serve to supply stereochemically well defined compounds. Therefore, it should be quite useful, and the number of examples is expected to increase in the future.

However, much work has to be done to correlate the ligand coupling, ligand exchange, and pseudorotation or turnstile rotation within hypervalent species formed by the nucleophilic attack on a central heteroatom of normal valency. Some work has already started, which will be reported elsewhere.