Ligand coupling reactions of hypervalent species

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Abstract. The concept of ligand coupling is explained and the actual examples
of many important reactions in which not only sulfur and phosphorus centered
hypervalent species, but iodine, silicon and copper centered hypervalent ones
are presented. It was also mentioned that many other reactions in which the
central metal atoms in the nickel triad elements are considered to behave as
the catalytic site for ligand coupling reaction, such as the Wäker process and
the Heck reaction.

Ever since we found the following reaction,(1) we have extended our concept of
ligand coupling(2) and have so many examples of these or similar reactions. However,
there were prior many reactions to enable us to postulate the concept.

A typical example of a three-centered, four electron bond, called a hypervalent bond
by Musher,(3) can be found in the substance in the structure of quaternary florinated
sulfur as demonstrated by X-ray analysis by Rundle et al.(4) and Pimentel, (5) in the
following figure. (Fig. 1)

The central atom in a hypervalent species is valence-shell-expanded and tends to
to extrude one pair of electrons to the normal valency of an octet. This is the driving
force of the reaction and there are three conceivable ways for hypervalent species to
collapse to form stable octet species; self-decomposition as exemplified by the well-
studied Wittig reaction,(6) ligand exchange,(7,8) and ligand coupling.(9-13) It is
well known that the equatorial ligands form sp\(^2\) and the axial linkages assume
p-orbitals. The axitlal bonds are longer and hold the electronegative substituents, as halogen while the equatorial ones are held with aromatic, olefinic and the negative groups, such as sulf oxide S-O bond. In dealing with the hypervalent species, one has to consider another physicochemical phenomenon, such as the tropological transformation, as BPR or TR. The following is the results of stereochemistry, when these hypervalent species are handled.

<table>
<thead>
<tr>
<th>Chemical Phenomenon</th>
<th>Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Ligand Exchange</td>
<td>inversion</td>
</tr>
<tr>
<td>+ (b) Ligand Coupling</td>
<td>retention</td>
</tr>
<tr>
<td>(c) Topological Transformation</td>
<td>retention or racemization</td>
</tr>
</tbody>
</table>

One of the driving force of ligand coupling is the following effective overlapping, shown by the sulfur-centered reaction, as illustrated below.

\[
\text{O} \quad \text{N} \quad \text{S-R}^+ \quad + \quad \text{MeMgBr} \quad \rightarrow \quad \sigma\text{-sulfurane} \quad \psi \quad \psi
\]

Meanwhile, the expression "reductive elimination" and "oxidative addition" are frequently used in organometallic chemistry. This term is also a mere description of the phenomenon and lacks mechanistic significance. The only two examples are show below.\(^{(14-15)}\)

\[
\text{R'}\text{R}_3 \quad \text{R}_1 \quad \text{R}_3
\]

Of course, prior to this assumption, there are many, many experiments and ideas.\(^{(16-39)}\)

Another example of stereochemistry is shown below.\(^{(40)}\) There is another example
is between optically active 1-phenylethyl 2-quinolyl sulfoxide and methylmagnesium bromide to afford completely retained 1-phenylethyl-2-quinoline in a high yield.\(^{(41)}\) In addition, there are a number of stereochemistry of geometrical isomers in the following ligand coupling reactions.\(^{(42)}\)

\[
\text{trans : cis} = 74:26
\]

\[
\text{trans : cis} = 74:26
\]

\[
\text{trans : cis} = 74:26
\]

\[
\text{trans : cis} = 74:26
\]

\[
\text{trans : cis} = 74:26
\]

In all the journals, we have found good many examples of ligand coupling reaction, but only a few which we or our friends carried out, are presented.\(^{(43-50)}\) We turn next to the ligand coupling on phosphorus atom. The stereochemistry of the ligand coupling on hypervalent phosphorus atom was carried out by Seyferth et al. accidentally in the following reaction\(^{(51)}\) The yields are good while the stereochemistry in both cases are nearly perfect.

\[
\text{trans : cis} = 74:26
\]

\[
\text{trans : cis} = 74:26
\]

\[
\text{trans : cis} = 74:26
\]

\[
\text{trans : cis} = 74:26
\]

\[
\text{trans : cis} = 74:26
\]

Many examples of the ligand coupling involving 2-pyridyl groups are summarized in the chart, as shown below.\(^{(52-55)}\) All these coupling reactions do not require

\[
*\text{Py} = \text{2-pyridyl}; R^1 = \text{2-pyridyl}, \text{Ph}; R^2 = \text{Me}, \text{Ph}, \text{PhCH}_2, 4-\text{MeC}_6\text{H}_4\text{CH}_2; M = \text{Li}, \text{MgX}.
\]
any alkaline condition (56) nor quaternary phosphorus compounds, as shown in the following reaction.

The uses of phosphorus trichloride, phosphorus oxychloride and thionyl chloride were found to undergo coupling reaction with many heterocycles (57) (Table. 1) The following examples are also interesting to note.

The involvement of 2-pyridyllithium in the ligand coupling is known in the following example (58).

Meanwhile, the following electrophilic substitution by chlorine was found to occur (59).

The use of the protic solvent is preferable. Chlorination, bromination, deuteration and diazocoupling are achieved, (60) as shown below. We believe that these are typical electrophilic substitutions, since the phosphorus atom in such a pentacoordinate species, especially 3-position of the axial pyridine ligand, is susceptical to the electrophilic substitution.

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We then turn to the hypervalent silicon species and only one example is sited below. (61,62)

What about the central iodine atom? There are so many and I do not want to go in detailed discussions but cite only a few examples.(63,64)

As we said earlier(2,30), many reactions involving organic copper reagents, such as the Ullmann type reaction shown below,(66) and the following one is a few typical example of the fast ligand coupling within the hypervalent copper(II) intermediate after a typical S_n2 process, as shown below.(67)

There are a number of examples of ligand coupling within hypervalent species of the nickel triad.(68) We are going to present only one stereospecific example to form the trans-acetoxyoxypalladium, eventually giving the final trans product.(69)
Another example is a typical Ullmann cross-coupling reaction shown below.\(^{(70)}\)

\[
\begin{align*}
\text{Cu, PdCl}_2(\text{PPh}_3)_2 (5 \text{ mol\%}) & \quad \text{DMSO, 130 °C} \\
810 \text{ S. OAE} & \quad \text{Another example is a typical Ullmann cross-coupling reaction shown below.} \quad \text{(70)} \\
\text{Acknowledgement.} \quad \text{Many colleagues have collaborated in pursuing this work.} \quad \text{Professors N. Furukawa, Y. H. Kim who is the chief organizer of this ICHAC-4} \\
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\text{comments and opinions of my friends who have kindly suggested in pursuing the} \quad \text{interesting works.} \\
\end{align*}
\]

\text{REFERENCES}

Ligand coupling in hypervalent species

50. S. Ogawa, private communications.
58. Y. Uchida, R. Kajita, Y. Kawasaki, S. Oae, Phosphorus, Sulfur and Silicon, 93(1-4) & 94(1-4) 403 (1994).