Mechanism of ligand coupling of hypervalent pentaarylantimony compounds*

Kin-ya AKIBA

Department of Chemistry, Faculty of Science, Hiroshima University
1-3-1 Kagamiyama, Higashi-Hiroshima 739, Japan

<u>Abstract</u>: Mechanism of ligand coupling reaction (LCR) of hypervalent pentaarylantimony compounds was investigated in benzene and in vapor phase (flash vacuum thermolysis). All the experimental results could be interpreted consistently by the idea invoking that the apical-apical coupling is the sole reaction path in the presence of stereoisomers which are inevitably generated by very fast Berry pseudorotation (BPR).

In order to obtain the above conclusion, the following experiments were carried out carefully: i) synthetic methods of pure mixed pentaarylantimony compounds were developed. ii) the structures of all $Tol_{5-n}SbAr_n$ were determined as TBP by X-ray analysis and were investigated in solution by using ^{13}C-chemical shifts of ipso-carbons of Tol and Ar groups. iii) ligand exchange (LE) was found to take place in benzene at 60 °C before any LCR started and relative stability (Si) of all the compounds was determined. iv) products of LCR in solution and in vapor phase were determined quantitatively.

Ab initio calculation for LCR of SbH_5 is also described.

I. Introduction

Ligand coupling reaction (**LCR**) is one of the fundamental reactions of hypervalent organic molecules of main group elements which cannot be realized for organic molecules of 2 nd row elements. After pioneering work of McEwen et al. which showed that LCR of pentaphenylantimony to afford biphenyl and triphenylantimony in benzene is a concerted and irreversible reaction (1), Hoffmann et al. carried out a theoretical investigation on the mechanism of LCR of phosphorane (PH_5) (2). They calculated the selectivity of the LCR and found that the coupling between the apical-apical ligands and the equatorial-equatorial ligands are symmetry allowed and that between the apical-equatorial ligands are forbidden. This was followed by some theoretical calculations and was essentially supported (3).

Hellwinkel et al. reported the LCR (ring-enlargement) of bis(biphenylene)methylphosphorane in 1976 (4) and Barton et al. investigated the ligand exchange (LE) and the LCR of tetraaryltellurium in 1980 (5). Recently, Oae's group has been reporting LCR of 2-pyridylsulfuranes generated *in situ* and some other examples, which should certainly be presented by his plenary lecture here (6).

There have been, however, only a few reports on the mechanism of LCR, although LCR is an essential reaction and is important theoretically and experimentally. This is due to the difficulty in finding out experimentally appropriate systems which undergo LCR by concerted and irreversible manner.

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* This paper is dedicated to celebrate the 65 th birthday of Professor Dr. Richard Neidlein of Pharmaceutical-Chemical Institute of Heidelberg University.

The model compounds such as R_5P and R_4S should suffer from very fast Berry pseudorotation (BPR) which makes it complicated and difficult to analyze experimental results. It is also required that any unshared electron pairs, which may certainly affect the reaction essentially, should not remain at the central atom and that any substituent should not contain heteroatom(s) which may influence the reaction path.

Here we report the experimental results on LCR of triarylbis(phenylethynyl)-antimony and pentaarylantimony compounds which meet the above criteria.

II.   LCR of Triarylbis(phenylethnyl)antimony

Because trimethylbis(propynyl)antimony is a TBP molecule and stable for handling (7), we prepared triarylbis(phenylethynyl)antimony and tried LCR in solid (8).

Scheme 1 shows the results that Ar-Ar is not formed at all and main product is bisacetylene and the yield of arylacethylene increases according to the electron-withdrawing ability of the Ar group. This is consistent with the idea that LCR takes place with the apical-apical substituents under very fast BPR.

76:24 (Ar=p-CH$_3$C$_6$H$_4$)
66:34 (Ar=Ph)
50:50 (Ar=p-ClC$_6$H$_4$)

PhC≡C-C≡CPh   PhC≡C-Ar   Ar-Ar
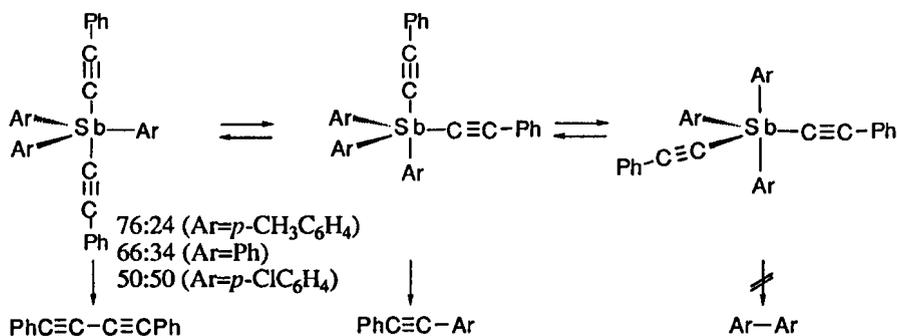
Scheme 1 Apical-apical coupling from trigonal bipyramidal Sb (V) to Sb (III)

III.   Synthesis and Structure of Mixed Pentaarylantimony Compounds

It was prerequisite to prepare **pure** Tol$_5$Sb and Ar$_5$Sb and also to develop new methods for the preparation of **pure** mixed pentaarylantimony compounds. This was successfully carried out as shown in Schemes 2 and 3.

Tol$_3$Sb $\xrightarrow{SO_2Cl_2}$ Tol$_3$SbCl$_2$ $\xrightarrow[\text{95\%}]{\text{4eq Tol-Li}}$ Li$^+$[Tol$_6$Sb]$^-$ $\xrightarrow{H_2O}$ Tol$_5$Sb 26%

Tol=p-CH$_3$C$_6$H$_4$

Ar$_3$Sb $\xrightarrow{Br_2}$ Ar$_3$SbBr$_2$ $\xrightarrow[\text{90\%}]{\text{3eq Ar-Li}}$ Li$^+$[Ar$_6$Sb]$^-$ $\xrightarrow{H_2O}$ Ar$_5$Sb 72%

Ar=p-CF$_3$C$_6$H$_4$
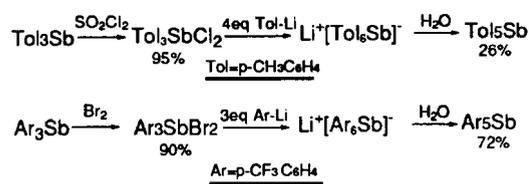
Scheme 2 Synthesis of Tol$_5$Sb and Ar$_5$Sb

Tol$_5$Sb $\xrightarrow[\text{61\%}]{Br_2}$ Tol$_4$SbBr $\xrightarrow[\text{79\%}]{KF}$ Tol$_4$SbF $\xrightarrow{ArMgBr}$ Tol$_4$SbAr 30%(purity>80%)

Tol$_2$SbCl $\xrightarrow[\text{13\%}]{ArLi}$ Tol$_2$SbAr $\xrightarrow{DAST}$ Tol$_2$SbArF$_2$ $\xrightarrow{TolMgBr}$ Tol$_4$SbAr 49%(purity>98%)

TolSbCl$_2$ $\xrightarrow[\text{30\%}]{ArLi}$ TolSbAr$_2$ $\xrightarrow{DAST}$ TolSbAr$_2$F$_2$ $\xrightarrow{TolMgBr}$ Tol$_3$SbAr$_2$ 65%(purity>98%)

Ar$_3$Sb $\xrightarrow[\text{90\%}]{Br_2}$ Ar$_3$SbBr$_2$ $\xrightarrow{TolMgBr}$ Tol$_2$SbAr$_3$ 30%(purity>98%)

SbF$_5$ $\xrightarrow[\text{64\%}]{\text{7eq ArLi}}$ Ar$_3$SbF$_2$ $\xrightarrow{TolMgBr}$ Tol$_2$SbAr$_3$ 58%(purity>98%)

Ar$_5$Sb $\xrightarrow[\text{66\%}]{DAST}$ Ar$_4$SbF $\xrightarrow{TolMgBr}$ TolSbAr$_4$ 67%(purity>98%)

Ar=p-CF$_3$C$_6$H$_4$ Tol=p-CH$_3$C$_6$H$_4$ DAST=Et$_2$NSF$_3$

Scheme 3 Synthesis of mixed pentaarylantimony compounds

The structure of all possible pentaarylantimony compounds were determined by X-ray analysis of single crystals and the essential feature is shown in TABLE 1. All compounds are TBP and the distortion from the ideal structure is negligible. The bond length of the apical substituent is **0.10 ± 0.01 Å** longer than the equatorial substituents.

Solution structures of the mixed pentaarylantimony compounds were also investigated using the ^{13}C chemical shifts of ipso carbons of the Ar and Tol groups as probes. It was concluded that almost the sole stereoisomer observed in solution at -80 °C has the same structure as in solid although BPR is very fast even at -80 °C.

TABLE 1. Structure of pentaarylantimony determined by X-ray analysis

Sb-C(1) apical	2.238	2.270	2.246	2.237	2.235	2.238
Sb-C(2) apical	2.254	2.233	2.256	2.248	2.255	2.240
Sb-C(3) equat	2.145	2.140	2.124	2.151	2.150	2.132
Sb-C(4) equat	2.151	2.142	2.131	2.135	2.144	2.148
Sb-C(5) equat	2.180	2.154	2.142	2.142	2.130	2.156

* Beauchamp et al., *Can. J. Chem.* **51**, 2952 (1973).

IV. Ligand Exchange of Pentaarylantimony Compounds

When a mixture of Tol_5Sb and Ar_5Sb in benzene was heated to effect LCR, unexpectedly we observed the appearance of mixed pentaarylantimony compounds at ca. 60 °C, i.e., LE took place for pentaarylantimony compounds where neither any unshared electron pairs nor halogens are present in the molecules. In order to determine the relative stability of pentaarylantimony compounds in solution a variety of mixtures of Tol_5Sb and Ar_5Sb in different molar ratios in benzene were heated at 60 °C to effect LE equilibrium, where LCR was not observed at all. Pure mixed pentaarylantimony compounds such as Tol_3SbAr_2 and Tol_2SbAr_3 were also used to see LE equilibrium, which gave the same equilibrium mixtures as 3:2 and 2:3 mixtures of Tol_5Sb and Ar_5Sb.

By comparison of the observed molar ratios of mixed pentaarylantimony compounds and the calculated statistic molar ratios, we could obtain relative stability constants (Si) of each pentaarylantimony compounds by dividing the former value by the corresponding value of the latter. Relative stability of each mixed pentaarylantimony compound in benzene at 60 °C was calculated as follows: Tol_3SbAr_2 (1.0) > Tol_2SbAr_3 (0.66) $\approx$ Tol_4SbAr (0.60) > Tol_5Sb (0.57) $\approx$ Ar_5Sb (0.58) > $TolSbAr_4$ (0.41).

TABLE 2. Relative Stability of Pentaarylantimony Compounds

T_5Sb	: T_4SbAr	: T_3SbAr_2	: T_2SbAr_3	: $TSbAr_4$	: $SbAr_5$
= t^5s_0 :	$5t^4as_1$:	$10t^3a^2s_2$:	$10t^2a^3s_3$:	$5ta^4s_4$:	a^5s_5

t / a	T_5Sb	T_4SbAr	T_3SbAr_2	T_2SbAr_3	$TSbAr_4$	$SbAr_5$
0.46	—	—	1.0	0.68	0.46	0.46
0.64	—	—	1.0	0.66	0.47	0.65
1.50	0.35	0.61	1.0	0.64	0.32	0.53 (·)
1.70	0.58	0.62	1.0	0.77	0.38	0.42
2.74	0.79	0.58	1.0	0.54	0.42	0.83
Si(av.)	(0.57)	0.60	1.0	0.66	0.41	0.58

Si= Relative Stability Constant of $T_{5-n}SbAr_n$ (·) is from T_3SbAr_2

V. Selectivity of Ligand Coupling Reaction of Mixed Pentaarylantimony Compounds

a) Benzene Solution at 220 °C

We tried to obtain the selectivity of LCR of each species of pentaarylantimony compound by determining quantitatively the products, i.e., Ar-Ar, Ar-Tol, and Tol-Tol, for each solution of Tol_5Sb and Ar_5Sb prepared to become in a different molar ratio. As mentioned above, LE equilibrium is attained before LCR takes place. Hence, it is necessary to take it granted for the analysis that LE equilibration is fast and the

equilibrium is maintained throughout the LCR and the rate of LCR is the same for each mixed pentaarylantimony compound. Under the assumptions we could calculate the relative yields of products for each species and are shown in TABLE 3 with the statistical values in parenthesis. It can be concluded that there is greater selectivity to afford Ar-Ar and Ar-Tol compared to that of Tol-Tol. This can be understood by invoking the apical-apical coupling under very fast BPR, although there are many factors involved and the support for the idea is still not strong enough here.

TABLE 3. Selectivity of LCR of pentaarylantimony compounds in benzene at 220 °C

	Tol_5Sb	Tol_4SbAr	Tol_3SbAr_2	Tol_2SbAr_3	$TolSbAr_4$	$ArSb_5$
Tol-Tol	100 (100)	0 ± 2 (60)	10 ± 6 (30)	2 ± 1 (10)	—	—
Tol-Ar	—	100 ± 2 (40)	2 ± 2 (60)	98 ± 9 (60)	21 ± 9 (40)	—
Ar-Ar	—	—	88 ± 25 (10)	0 ± 8 (30)	79 ± 9 (60)	100 (100)

Values in parenthesis are statistical values without selectivity
$Tol = p\text{-}CH_3C_6H_4$ $Ar = p\text{-}CF_3C_6H_4$

b) Flash Vacuum Thermolysis

In order to simplify the system and also to certify that LCR takes place from **only one species** of mixed pentaarylantimony compound, we have investigated a variety of experimental conditions for flash vacuum thermolysis and found satisfactory conditions. The yields of Ar-Ar (%) and Ar-Tol (%) are shown together with possible stereoisomers by BPR in Scheme 4. Under the conditions, the extent of LE of the residual sample which did not vaporize was determined to be less than 5% except for Tol4SbAr, the rate of LE was exceptionally fast and Ar-Ar (19%) and Tol-Tol (14%) were obtained which should be produced from Tol3SbAr2 and Tol5Sb. The yields of mixed triarylantimony compounds were also determined by glc and the results essentially corresponded to the yields of Ar-Ar and Ar-Tol for each starting material.

One of the most important results is that **Tol-Tol was not detected** from TolSbAr4, Tol2SbAr3 and Tol3SbAr2. This should mean that **the equatorial-equatorial coupling does not take part for unimolecular LCR**. The yield of Ar-Ar is enhanced by the death of Tol-Tol and by the decrease of Ar-Tol. This can be interpreted by the idea that **LCR takes place solely by the apical-apical coupling** of two kinds of stereoisomers in equilibrium under very fast BPR. This is consistent with the results of triarylbis(phenylethynyl)antimony.
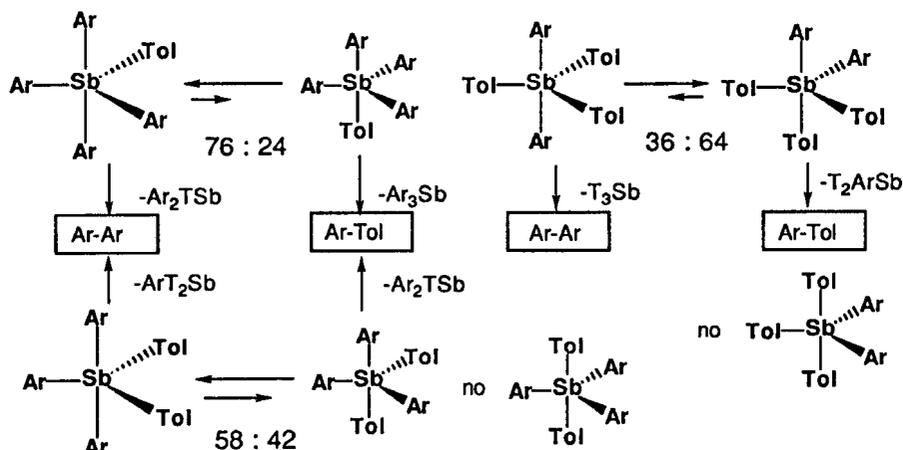

Scheme 4 Apical-apical coupling from pentaarylantimony compounds

c) Catalyzed LCR of Pentaarylantimony Compounds

LCR of pentaarylantimony compounds was accelerated by cationic species such as LiBAr'$_4$ [Ar'=3,5-(CF$_3$)$_2$C$_6$H$_3$] and also Cu(acac)$_2$. The yields of coupling products were almost the same as shown in Scheme 4 and the same kind of interpretation is also valid.

VI. *Ab initio* Calculation of BPR and LCR of SbH$_5$

Advanced *ab initio* calculation was applied to BPR and LCR of SbH$_5$ and the results are illustrated in Scheme 5 (9).
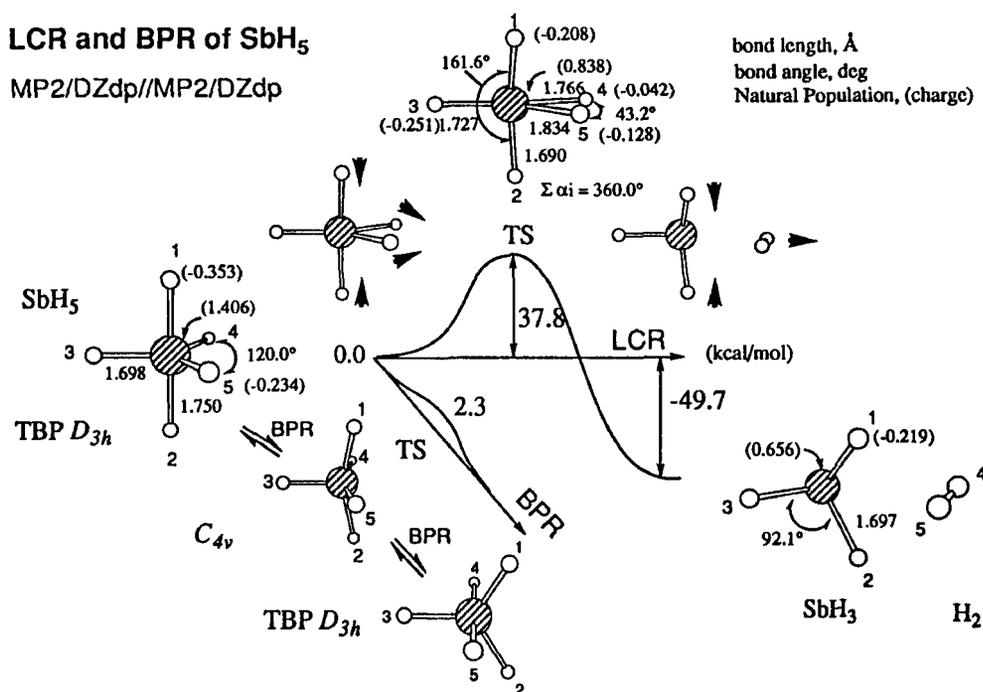
Scheme 5 *Ab initio* calculation of BPR and LCR of SbH$_5$

This predicts that the LCR of SbH$_5$ takes place with the equatorial-equatorial substituents through quite unique transition state although this result cannot discriminate the apical-apical coupling because there is very fast BPR. Anyway, this is contradictory to the experimental results presented here.

Selectivity for LCR of SH$_4$ is also calculated by *ab initio* method and is predicted that the LCR goes through a very polar transition state by the apical-equatorial coupling (10).

VII. Conclusion

Our total experimental results on LCR of pentaarylantimony compounds can best be interpreted by the idea invoking that the apical-apical coupling is the sole reaction path in the presence of stereoisomers which are inevitably generated by very fast BPR. Apical substituents should be responsible for LCR of 5-coordinate hypervalent molecules because the bond energy of the apical bond should be considerably weaker than that of the equatorial one. The result is explained by the **memory effect** of the apical substituents which implies that once the apical substituents start bending motion for LCR the combination of the substituents is kept through the transition state to the final products. Further theoretical study is necessary to make it clear what is the essential reason for the present contradiction.

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