Syntheses, Crystal and Solution Structures, Ligand Exchange, and Ligand Coupling Reactions of Mixed Pentaarylantimony Compounds

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Abstract: All the possible combinations of mixed pentaarylantimony compounds bearing *p*-methylphenyl and *p*-trifluoromethylphenyl groups were synthesized, i.e., $Ar_nTol_{5-n}Sb$ (n = 0-5: Ar = *p*-$CF_3C_6H_4$, Tol = *p*-$CH_3C_6H_4$): Tol_5Sb (**1**), $ArTol_4Sb$ (**2**), Ar_2Tol_3Sb (**3**), Ar_3Tol_2Sb (**4**), Ar_4TolSb (**5**), and Ar_5Sb (**6**). Compounds **2**-**5** are the first well-characterized examples of mixed acyclic pentaarylantimony species. The structures of **2**-**6** were determined by X-ray crystallography to

bear trigonal bipyramidal (TBP) geometry with the more electronegative *p*-trifluoromethylphenyl substituents selectively occupying the apical positions. Considerations based upon the chemical shifts of the ipso carbons of the aryl and the tolyl groups suggested that the solution structures of **1**–**6** were also TBP although pseudorotation of them could not be frozen even at −80 °C. Ligand exchange reactions (LERs) were found to take place between **1** and **6** at ca. 60 °C in [D$_6$]benzene and all the six species **1**–**6** were found in the equilibrium mixture. The relative stabilities of **1**–**6** were determined quantitatively by comparison of the observed molar ratios of **1**–**6** in equilibrium with calculated statistical molar ratios, and Ar_2Tol_3Sb (**3**) was found to be the most stable. The ligand coupling reactions (LCRs) from **2**–**5** in solution were found to be greatly accelerated by adding $Cu(acac)_2$ or Li^+TFPB^- [TFPB: $B(3,5\text{-}(CF_3)_2C_6H_3)_4$], with the rate becoming comparable with the LER. The use of flash vacuum thermolysis (FVT) allowed the LCR to occur with very little ligand exchange except in the case of $ArTol_4Sb$ where it was very fast. The selectivities of LCRs determined by the yield of the formed biaryls by FVT were highly consistent with those in the catalyzed reactions in solution, where bitolyl was not obtained at all. The experimental results suggested that the LCR of pentaarylantimony compounds proceeds in the manner of apical-apical coupling.

Introduction

Hypervalent compounds of group 15 elements have been extensively investigated in terms of structure, permutational behavior, and reactions.[1] Especially, pentacoordinate phosphorus chemistry has unveiled important properties of hypervalent compounds.[2] Notable basic properties among them are apicophilicity[3,4] and pseudorotation.[5] The former is the relative preference for a substituent to occupy an apical position of trigonal bipyramidal (TBP) structures, and electronegative groups are generally favored in apicophilicity. The latter is a stereomutation mechanism of TBP molecules, and this process is generally very fast and is called Berry pseudorotation. In comparison to phosphorus, however, hypervalent antimony chemistry has still been less studied,[1,6] therefore it is quite interesting to clarify its fundamental properties.

The ligand coupling reaction (LCR) is one of the fundamental reactions of hypervalent organic molecules of main group elements and the selectivity in the LCR of 10-M-5[7] (M: group 15 elements) compounds has attracted interest in relation with the bonding scheme which differs greatly with compounds of ordinary valency such as tetravalent compounds. Tetravalent compounds usually hold sp^3 or sp^2 hybrid orbitals and therefore there is no distinction in the nature of the bonds concerning coupling reactions. However, for 10-M-5 compounds of which there are two possible geometries, TBP structure and square pyramidal (SP) structure, there are usually two kinds of bonds, that is, two apical and three equatorial bonds in the TBP and one axial and four basal bonds in the SP.[6] Theoretical investigation on the mechanism of the LCR of phosphorane (PH_5) was first carried out by Hoffmann et al.,[4a] who concluded that the LCR between the apical-apical ligands and the equatorial-equatorial ligands from TBP structures were symmetry allowed and that between the apical-equatorial ligands was forbidden (Scheme 1). Although the symmetry forbidden apical-equatorial coupling process was once reported to be favored,[8] recent calculation essentially support the conclusion by Hoffmann and the equatorial-equatorial coupling was calculated to be the lowest energy process for PH_5, AsH_5, and SbH_5,[9-12] although the apical-equatorial process was calculated to be favored for BiH_5.[11] Experimentally, the LCR of bis(biphenylene)methylphosphorane,[13] tetraaryltellurium,[14] 2-pyridylsulfuranes (generated in situ),[15] pentavalent oxathietane,[16] and pentavalent oxastibetane[17] have been reported, however, the essential nature of the selectivity of LCR has yet to be discussed. We have already reported on the LCR of triarylbis(phenylethynyl)antimony(V) compounds for this purpose and found that no biaryls were formed from the LCR (Table 1). However, the instability of these compounds prevented detailed examination.[18] A suitable system for investigating the selectivity of the LCR experimentally should fulfill the following requirements: (i) the LCR should take place in a concerted manner; (ii) the reverse reactions from the products should not take place; (iii) the system should be sterically unbiased; (iv) the structure of the starting compounds should be unambiguous (hopefully determined by X-ray analysis).

<Scheme 1>

<Table 1>

Pioneering work by McEwen showed that the LCR of ^{14}C-labelled pentaphenylantimony in unlabelled benzene afforded biphenyl bearing ^{14}C-labels for both phenyl rings and ^{14}C-labelled triphenylantimony. Neither ^{14}C-labelled benzene nor biphenyl having ^{14}C-label for only one of the two phenyl rings was formed. Thus, this LCR was confirmed to take place concertedly (Scheme 2).[19] Thus, mixed pentaarylantimony compounds having different carbon substituents, which are electronically different but sterically similar, would be good candidates for the examination of the LCR since the reverse reaction from biaryls and triarylantimony compounds to form pentaarylantimony compounds is not a conceivable process. To this end, we chose to examine mixed pentaarylantimony(V) species, $Ar_{n}Tol_{5-n}Sb$ (n = 1-4: Ar = p-$CF_3C_6H_4$, Tol = p-$CH_3C_6H_4$).

<Scheme 2>

<Scheme 3>

Here we report on the syntheses and the structural determination of a series of mixed pentaarylantimony compounds, $Ar_{n}Tol_{5-n}Sb$ (n = 0-5) **1**-**6**. Structures in the solid state were determined by X-ray crystallographic analyses and those in solution were estimated by ^{13}C NMR. TBP structure was suggested for both cases. The ligand exchange reaction was found to take place in solution because a mixture of Tol_5Sb (**1**) and Ar_5Sb (**6**) in benzene at 60 °C showed the presence of **1**-**6** in equilibrium (Scheme 3). Relative stabilities of **1**-**6** were estimated by observing the molar ratios of them in a certain mixture of **1** and **6** in benzene (60 °C). In the equilibrium, Ar_2Tol_3Sb (**3**) was found to be the most stable compound among these species. Finally, selectivities of ligand coupling reaction (LCR) of each **2**–**5** catalysed by LiTFPB in solution as well as those obtained by flash vacuum thermolysis (FVT) are presented and the mechanism of LCR will be discussed.

Results and Discusion

Preparation of Tol_5Sb (1), $ArTol_4Sb$ (2), Ar_2Tol_3Sb (3), Ar_3Tol_2Sb (4), Ar_4TolSb (5), and Ar_5Sb (6) (Ar = *p*-$CF_3C_6H_4$, Tol = *p*-$CH_3C_6H_4$).

The preparation of pentakis(*p*-methylphenyl)antimony (**1**) has already been reported.[20,21] Pentakis(*p*-trifluoromethylphenyl)antimony (**6**) was prepared as shown in Scheme 4. Specifically, Ar_3Sb (**8**) was prepared from antimony trichloride (**7**) and ArMgBr,[22] but ArLi gave higher yields. Stibine **8** was dibrominated to give **9** in a good yield. The reaction of the dibromide **9** with 2 eq of ArLi gave Ar_5Sb (**6**). However, in order to obtain "super pure" **6**, it was necessary to use an excess amount of ArLi to form ate complex $[Ar_6Sb]^-Li^+$, and the precipitated ate complex was washed with *n*-hexane under argon and was decomposed with water to give pure **6**. Tol_5Sb (**1**) was also obtained in pure form by the similar procedure through $[Tol_6Sb]^- Li^+$.

<Scheme 4>

The synthesis of the mixed compounds **2**–**5** was more difficult and needed laborious operations. For mixed pentaarylbismuth compounds, Seppelt[23] reported the synthesis by the use of triarylbismuth dihalides and aryllithium as the starting materials. We tried to apply this method to the preparation of **2**–**5**, but found it very difficult to obtain pure compounds. A variety of reaction conditions using TolLi and ArLi with triarylantimony dihalides (Br, Cl, F) were examined. However, mixtures of **2**–**5** were almost always obtained. The reason is the ability of pentaarylantimony compounds to readily form ate complexes (Scheme 5). This means that the desired pentaarylantimony compounds form ate complexes with the excess organolithium reagents and undergo ligand exchange reactions in situ via the ate complexes. Mild reaction conditions (−78 °C), shortening of the reaction time and changing the solvents had only a minor effect to form the desired pentaarylantimony.

<Scheme 5>

Doleshall et al. showed that tetraphenylantimony fluoride reacts with methylmagnesium iodide in a very clean fashion to give methyltetraphenylantimony.[24] Therefore, this strategy to use antimony(V) fluorides and Grignard reagents was applied to the syntheses of **2**–**5**.

We found that only a combination of TolMgBr and antimony fluorides gave satisfactory results, whereas the use of ArMgBr was not useful (vide infra). Therefore, four fluorides, Ar_4SbF (**10**), Ar_3SbF_2 (**12**), $Ar_2TolSbF_2$ (**15**) and $ArTol_2SbF_2$ (**18**) to be reacted with TolMgBr, were necessary for the synthesis of **2** to **5**. Ar_4SbF (**10**) is easily available by treatment of Ar_5Sb (**6**) with diethylaminosulfur trifluoride (DAST) (Scheme 6).[25] This reaction is similar to the known halogenation of pentaarylantimony compounds by Cl_2, Br_2 or I_2.[26] The arylation of **10** with TolMgBr proceeded smoothly to give Ar_4TolSb (**5**) in good yield (Scheme 6). The preparation of Ar_3SbF_2 (**12**) was found to be even easier. In an attempt to prepare Ar_5Sb (**6**) directly from antimony pentafluoride (**11**) with 7 equiv of ArLi, we incidentally isolated **12** in 64% yield by usual workup with water. This method is superior to the published method.[27] Compound **12** was converted to Ar_3Tol_2Sb (**4**) with TolMgBr in 58% yield (Scheme 7).

<Scheme 6>

<Scheme 7>

The preparation of the mixed fluorides $Ar_2TolSbF_2$ (**15**) and $ArTol_2SbF_2$ (**18**) was more troublesome. First, Ar_2TolSb (**14**) was prepared by the reaction of ArLi with $TolSbCl_2$ (Scheme 8). Although we used repeatedly recrystallized $TolSbCl_2$, which appeared to be very pure based on ^1H NMR analysis, the formation of 3-4% of Ar_3Sb (**8**) as a byproduct was inevitable probably due to contamination with a small amount of $SbCl_3$. However, **8** could be removed by preparative HPLC to give **14**. Fluorination of **14** with DAST gave **15**, which was highly soluble in almost all organic solvents, but could be recrystallized from a small amount of methanol to give white needles. Subsequent arylation with TolMgBr gave **3** in 55% yield (Scheme 8).

<Scheme 8>

$ArTol_4Sb$ (**2**) was prepared in essentially the same way. The preparation of Tol_2SbCl from Tol_3Sb (**16**) and $SbCl_3$ (**7**) was tried repeatedly according to procedures described for Ph_2SbCl.[28] However we found that a large amount of byproducts like $TolSbCl_2$ and Tol_3SbCl_2 were always formed and we were not able to isolate Tol_2SbCl in pure form by recrystallization although various solvents were examined. We arylated, therefore, the crude reaction mixture with ArLi, then separated crude $ArTol_2Sb$ (**17**) by preparative HPLC. Recrystallization of the separated product from methanol gave pure $ArTol_2Sb$ (**17**) although in a low yield

(8%). Fluorination was again achieved with DAST to give a yellowish oil of **18**, which was used in the following arylation to give the desired product **2** in 49% yield (Scheme 9).

<Scheme 9>

All in all, the desired pentaarylantimony(V) compounds **2**–**5** were successfully prepared by the use of TolMgBr in good yields (Schemes 6-9, and entries 1-4 in Table 2). However, the reaction conditions had to be controlled carefully to avoid the redistribution reaction as shown in Scheme 5. In order to obtain good results, it was necessary to carry out the reaction at 0 °C with vigorous stirring and to quench the mixture with water within 20 min. Prolonged reaction time caused the ligand exchange reaction. The mixed pentaarylantimony compounds are thermally stable if they are prepared pure and they behave like usual homoleptic pentaarylantimony compounds. However special care is necessary in handling $\mathrm{ArTol_4Sb}$ (**2**) because the compound is very sensitive to the LER and the reaction proceeds somewhat (ca. 5%) even during recrystallization from dry benzene in the refrigerator over a several day period. It should also be mentioned that the melting points of **2**–**5** depends very much on the speed of heating because LER takes place during the measurements.

Furthermore we tried to prepare $ArTol_4Sb$ (**2**) using ArMgBr and Tol_4SbF. However, it was found that the reaction did not give pure **2** (entries 5-7 in Table 2). It is quite remarkable that only the combination of a fluoride with a reactive Grignard reagent (TolMgBr) is satisfactory for the preparation of pure products in acceptable yields. As evident by the comparison of entries 2 and 8 in Table 2, the fluoride was obviously superior to the bromide as the electrophile. We believe that having a fluorine instead of a bromine makes the antimony atom more electrophilic, probably because fluorine coordinates with magnesium salts, and hence nucleophilic attack on the antimony atom by Grignard reagents is accelerated.

<Table 2>

X-Ray Structures of 2-6. The structures of pentacoordinate compounds of group 15 elements have attracted interest even in recent years.[1,2,6] Pentaaryl derivatives of phosphorus and arsenic compounds generally prefer TBP structures if they are not influenced by chelating ligands.[29] In contrast, pentaarylbismuth compounds most frequently adopt the SP geometry.[23] Antimony compounds seem to be a borderline case as shown in the well-known SP structure of Ph_5Sb[30] and the TBP structure of Tol_5Sb[20] and $Ph_5Sb \cdot 0.5C_6H_{12}$.[31] In addition, the influence of the para substituents on the apicophilicity in TBP structures is also a major concern. Although the apicophilicity of ligands attached to pentacoordinate phosphorus has attracted much attention[3,4] due to the important role of phosphorus in biological systems,[32] apicophilicity for its higher homologues and for compounds having substituted phenyl groups has not been examined to depth. Thus, the investigation of the X-ray structures of the mixed pentaarylantimony compounds would be of intriguing interest.

Suitable crystals were obtained by recrystallization from benzene-acetonitrile (**2**, **3**, **4**, and **6**) or diethyl ether-acetonitrile (**5**). Figures 1-5 show the ORTEP drawings of **2**-**6**, and Table 3 shows selected bond lengths and angles around the antimony atom together with reported data for **1**,[20] and the ***D*** angle which has been defined by Seppelt and was calculated from the structural data. The ***D*** angle is the difference between the two largest angles involving the central atom and two ligands in a pentacoordinate main group element compound and serves as a parameter for indicating the degree of progress of the Berry pseudorotation process (***D*** = 0-15° sp; ***D*** = 45-60° tbp).[23] All the determined structures clearly assumed TBP structure like **1**.[20] Two independent molecules were observed for **6**. Since the apical positions in **2**-**5** are selectively occupied by the Ar groups, it is obvious that the apicophilicity of the Ar group is higher than that of the Tol group as expected.

<Figure 1>

<Figure 2>

<Figure 3>

<Figure 4>

<Figure 5>

The bond lengths between Sb and the ipso carbon atoms of the equatorial ligands {C(15), C(22) and C(29)} were all in the range of 2.13-2.16 Å. The three ligands are tilted in order to avoid steric hindrance. The apical bonds were also of similar length among each other {C(1) and C(8)} (2.23-2.26 Å), and they were slightly longer (by ca. 0.10 Å) than the equatorial bonds. No significant differences between the Sb-C(Ar) and Sb-C(Tol) distances were observed even though the electronic property of Ar and Tol groups are different. Bond angles conform to the essential character of TBP structure.

<Table 3>

The measured structures **2**, **3**, **4**, **5** and **6** have ***D*** angles between 47.8 and 55.4° which indicate that these are all TBPs although they are somewhat distorted from the ideal TBP (***D*** = 60°). The exclusive adoption of TBP structure for these compounds is somewhat surprising. Even though **1** was reported to bear a likewise TBP structure with ***D*** = 48°,[20] the structure of Ph_5Sb (***D*** = 14.8°)[30] clearly has shown the possibility for some pentaarylantimony compounds to adopt the SP structure as well. The trend for preferring the TBP structure finds some support from an effect observed by Seppelt.[23] He determined the structures of a variety of pentaarylbismuth derivatives and found that whenever an aryl group possessed a para substituent, the structure tended to be more of a TBP. However, this trend was not so demanding for all of the compounds and was also dependent on the nature of the central elements, as exemplified by Ph_5Bi (***D*** = 13°) and Tol_5Bi (***D*** = 35°).[23] It could be that due to the bulkiness of the methyl and trifluoromethyl groups in comparison with hydrogen, we believe that they cause changes in the lattice energies and make the TBP structure more favorable for antimony compounds than for bismuth compounds.

Structures of 1-6 in Solution. Not much is known about the solution structure of pentaarylantimony compounds due to the rapid pseudorotation of pentacoordinated hypervalent molecules. Actually, for the compounds bearing multiple Ar groups (**3**–**6**), only one CF_3 signal for each compound was observed by ^{19}F NMR spectroscopy even at −80 °C as well as only one ipso carbon resonance for all of the Ar groups in each compound by ^{13}C NMR.

Reich published a noteworthy paper on the ^{13}C NMR spectroscopy of a mixture of pentaorganotin ate complexes $[Ph_nMe_{5-n}Sn]^- Li^+$.[33] In his examination, the chemical shifts of the ipso carbons and the $^{119}Sn-^{13}C_{ipso}$ coupling constants strongly supported the assumption that these complexes adopt TBP geometry in solution, and the chemical shift values for the apical and equatorial carbon atoms were estimated from the averaged ipso carbon resonances. This seemed to be a promising method for the otherwise difficult to determine solution structure of pentacoordinate main group element compounds highly flexible due to rapid BPR. We employed this method to determine the solution structures of **1**–**6**. ^{13}C NMR spectra were recorded in $[D_8]$toluene and assignments of all the ipso carbons of **1**-**6** were carefully made on the basis of H-H COSY, C-H COSY and C-H long-range COSY spectra.

Figure 6 shows the chemical shifts of the ipso carbons of the Ar and the Tol groups at −80 and 60 °C along with Reich's data of the tin ate complexes. The general trend for the Ar chemical shifts at −80 °C appeared to be very similar to those of Reich's data. The ipso carbons of the Ar groups in **2** and **3** at −80 °C have about the same chemical shifts (δ= 162.9 ppm in **2**, δ= 161.3 ppm in **3**). Assuming that these compounds take on TBP structure in the ground state, the Ar group(s) of **2** and **3** should mainly occupy the apical position(s) at −80 °C because of their electron-withdrawing nature. Therefore, the chemical shift of the Ar ipso carbon at the apical position (δ_{ap}) is estimated to be 161.3 ppm based on the chemical shifts of **3**, which is expected to have the least distorted TBP geometry in solution among the mixed pentaarylantimony compounds **2**-**5**.

<Figure 6>

The averaged ipso ^{13}C chemical shift of the Ar group can be calculated to be $\delta_{\mathrm{Ar}} = (a\delta_{\mathrm{ap}} + e\delta_{\mathrm{eq}})/(a + e)$ where δ_{ap} (= 161.3 ppm) and δ_{eq} are intrinsic chemical shift of Ar group at apical and equatorial positions and a is the number of Ar ligand in the apical positions and e is that in the equatorial positions. In **6** where all positions are occupied by the Ar groups, the averaged chemical shift (δ_{Ar}) of the ipso carbon (δ = 148.9 ppm) should be equal to $(2\delta_{\mathrm{ap}} + 3\delta_{\mathrm{eq}})/5$. Thus, δ_{eq} can be calculated to be 140.7 ppm. Based on these values of δ_{ap} and δ_{eq}, the chemical shifts of the corresponding carbon of **4** and **5** are calculated to be 154.4 ppm $\{(2\delta_{\mathrm{ap}} + \delta_{\mathrm{eq}})/3\}$ and 151.0 ppm $\{(2\delta_{\mathrm{ap}} + 2\delta_{\mathrm{eq}})/4\}$, respectively, which are consistent with the observed values for **4** (155.3 ppm) and **5** (152.0 ppm). Thus, the assumption of TBP structure seems to be legitimate. The chemical shifts of the ipso carbons of the Tol group show in general the same behavior as that of the ipso carbons of the Ar group. By the same token, $\delta_{\mathrm{ap,Tol}}$ and $\delta_{\mathrm{eq,Tol}}$ were estimated to be 155.5 and 135.5, respectively, at −80 °C.

The equilibrium between positional isomers in pentacoordinate main group elements is considered to be temperature dependent. The plots of the chemical shifts of the ipso carbons of the both Ar and Tol groups of **1**–**6** at the highest measured temperature of 60 °C clearly show that the characteristic bent shape observed at −80 °C has diminished to become almost linear (Figure 6). The chemical shifts at 60 °C mainly depends on the number of Ar (or Tol) groups without concerning its position (apical or equatorial), indicating that the apicophilicity of Ar and Tol group should be almost the same at 60 ˚C. This means that the rate of pseudorotation is fast at 60 ˚C being Ar or Tol group indiscriminate and that is slow at −80 ˚C being Ar or Tol group in equilibrium position according to apicophilicity.

Disproportionation Reaction. In order to certify that no intermolecular reaction takes place during the LCR, we heated a mixture of **1** and **6** in [D_6]benzene at 60 °C. Contrary to our expectations, five peaks which were identified as those for

2–**6** by comparison with the authentic samples appeared in ^{19}F NMR. Occurrence of equilibration among **1**–**6** by the LER was unexpected because there are neither lone pair electrons nor halogens on the antimony atom.[34,35] It took several days for the equilibration to come to completion although the rate was drastically dependent on the purity and on the concentration of the samples. When a small amount of Ar_4SbBr or Ar_4SbCl was added to the system the reactions were greatly accelerated probably because the stibonium ion promotes aryl group transfer via the mechanism shown in Scheme 10. When we used "super pure" samples of **1** and **6**, it took up to two or three weeks for completion of the equilibration at the same temperature, although the rate was still dependent on the concentration of the solution. In these cases a mechanism in which concommitant mutual exchange of aryl groups via a dimeric complex involving pseudohexacoordinate antimony might be operative as shown in Scheme 11. However, the equilibrium ratio was not dependent on the purity of the samples or the concentration of the solution. Hence Tol_3Sb and Ar_3Sb do not affect the equilibration at all, and the LER can be considered to be a characteristic reaction for the hypervalent bond.

<Scheme 10>

<Scheme 11>

In order to determine the relative stability of pentaarylantimony compounds in solution, a variety of mixtures of $\mathrm{Tol_5Sb}$ (**1**) and $\mathrm{Ar_5Sb}$ (**6**) in differing molar ratios in [D_6]benzene were heated at 60 °C to effect the ligand exchange equilibrium, where the ligand coupling reaction was not observed at all. The experimental relative ratio was determined by the use of signal integrals in ^{19}F NMR. The statistical (theoretical) molar ratios in equilibrium were calculated by the following equations derived by the use of combinatorial theory (eq. 1):

$$\begin{gathered}\mathrm{Tol_5Sb} : \mathrm{ArTol_4Sb} : \mathrm{Ar_2Tol_3Sb} : \mathrm{Ar_3Tol_2Sb} : \mathrm{Ar_4TolSb} : \mathrm{Ar_5Sb} \\ = {}_{5tN_A}C_5 : {}_{5tN_A}C_4 \times {}_{5aN_A}C_1 : {}_{5tN_A}C_3 \times {}_{5aN_A}C_2 : {}_{5tN_A}C_2 \times {}_{5aN_A}C_3 : {}_{5tN_A}C_1 \times {}_{5aN_A}C_4 : {}_{5aN_A}C_5 \\ \approx t^5 : 5t^4a : 10t^3a^2 : 10t^2a^3 : 5ta^4 : a^5 \qquad (1)\end{gathered}$$

(*a*: initial mole of $\mathrm{Ar_5Sb}$, *t*: initial mole of $\mathrm{Tol_5Sb}$, N_A: Avogadro's number)

The experimental ratio of Tol_5Sb, which cannot be observed in ^{19}F NMR, was calculated by subtracting the amount of **2**–**6** from the total of 10-Sb-5 compounds. By dividing the observed molar ratio by the calculated statistical molar ratio of each mixed pentaarylantimony compound, the relative stability constant (S_i) of each pentaarylantimony was calculated. One example is shown for the case of t/a = 2.74, where t = the initial amount of the Tol_5Sb (**1**) and a = the initial amount of the Ar_5Sb (**6**) and the equilibrium ratios were normalized against Ar_2Tol_3Sb (**3**) (S_2 =1.0) which is the most stable compound (Table 4). In this case, the quantity of

<Table 4>

6 was very small, and thus the stability constants for **6** potentially contains large experimental error. Since the observed ratio of **1** relies on the accuracy of **2**–**6**, it follows that the stability constant for **1** also may contain large error. Table 5 shows the relative stability constants for **1**–**6** obtained by the use of mixtures in differing molar ratios of **1** and **6** (entries 1-3, 5, 6). Pure Ar_2Tol_3Sb (**3**: *t*/*a* = 1.50) was also used to see whether the ligand exchange equilibrium occurs even for pure compounds, too. This gave stability constants consistent with those from the mixture of **1** and **6** (Table 5 entry 4). All the data clearly show that Ar_2Tol_3Sb (**3**) is the most stable compound. The relative stability constants for **1**-**6** obtained in each entry of Tabel 4 should be the same value a priori. The large ambiguity in **1** stems from the fact that **1** cannot be directly observed in ^{19}F NMR and the amount of **1** was estimated from the quantity of other compounds as described above, and that in **6** is due to the fact that the quantity of **6** was extremely small. However, the order of stability could be determined as follows: Ar_2Tol_3Sb (**3**, 1.0) > Ar_3Tol_2Sb (**4**, 0.71±0.13) > $ArTol_4Sb$ (**2**, 0.54±0.09) > Ar_4TolSb (**5**, 0.42±0.07) (Table 5). The reason for **3** being highest in stability can be clearly explained by invoking the electron-donating property of the three equatorial *p*-methylphenyl groups and the electron-withdrawing property of the two apical *p*-trifluoromethylphenyl groups. The stability order shows that both the replacement of one equatorial Tol group for Ar to make up **4** and vice versa to make up **2** results in a decrease in relative stability. Further substitution of Tol for Ar in **4** to make up **5** led to even lower stability.

<Table 5>

Uncatalyzed ligand coupling reactions (LCRs) from mixed pentaarylantimony compounds in solution: LCR from the equilibrated mixture of mixed pentaarylantimony compounds: As discussed above, we found that the LER took place at much lower temperatures (ca. 60 ˚C) than the LCR (ca. 160 ˚C). Therefore, we initially examined the LCR from equilibrated mixture of the mixed pentaarylantimony compounds (Scheme 12). For a mixture of Ph_5Sb and Tol_5Sb (**1**), the ratio of the ligand coupled products, biaryls, were almost identical with the statistical ratio (Figure S1: see Supporting Information). This result was consistent with that reported on similar LCRs from a mixture of Ph_4Te and Tol_4Te.[14] However, upon the use of a mixture of Tol_5Sb (**1**) and (*p*-ClC_6H_4)$_5$Sb, the ratio of the products became notably different from the statistical ratio in preference for the formation of (*p*-ClC_6H_4)-Tol (Figure S2: see Supporting Information). In the case of Tol_5Sb (**1**) and (*p*-$CF_3C_6H_4$)$_5$Sb (**6**) the preference for the formation of Tol-Ar by the sacrifice of Tol-Tol became more apparent (Figure 7).

<Scheme 12>

<Figure 7>

Since ^{19}F NMR is easy to monitor, we chose (*p*-$CF_3C_6H_4$)$_5$Sb (**6**) for investigating the LCR with the hope to calculate selectivities in the LCR from a mixture of Tol_5Sb (**1**) and Ar_5Sb (**6**) in differing molar ratios in [D_6]benzene. As mentioned above, LE equilibration was much faster than the LCR in solution. However, it would be possible to determine the LCR selectivity from product distribution if the following two requirements were met during measurements: (i) LE equilibration was fast and equilibration was maintained throughout the LCR, and (ii) the rate of the LCR was the same for all of the mixed pentaarylantimony compounds. Monitoring the LCR with ^{19}F NMR revealed however that the rate of the LCR from compounds having more Ar groups (such as **5** and **6**) were much slower than those from Tol_5Sb (**1**) or $ArTol_4Sb$ (**2**). Therefore, the fundamental assumptions of (ii) and certainly also (i) could not be maintained, hence quantitative calculation of the selectivity from each compound was not possible under uncatalyzed conditions.

Catalyzed LCR from $Ar_nTol_{5-n}Sb$ in solution: Acceleration of LCR by $Cu(acac)_2$ and Li^+TFPB^- [TFPB: $B(3,5\text{-}(CF_3)_2C_6H_3)_4$]: In order to determine the selectivity of the LCR for each pentaarylantimony, it was necessary to find experimental conditions which allow only one species of mixed pentaarylantimony compounds to take part in the LCR. With all the possible mixed pentaarylantimony compounds in hand, we sought suitable conditions for facile LCRs using catalysts. $Cu(acac)_2$ has been reported to accelerate the LCR of Ph_5Sb,[35] however, there was a chance that transmetallation of the phenyl group to the copper atom could not be avoided. Therefore, we also searched for catalysts capable of accerelation without the possibility of transmetallation. We found that anhydrous Li^+TFPB^- [TFPB: $B(3,5-(CF_3)_2C_6H_3)_4$] was a very good catalyst for the purpose, whereas LiBr and LiCl were not effective at all. Anhydrous LiTFPB was synthesized by Sonoda et al and was reported to be a very powerful catalyst for some Diels-Alder reactions.[36] The catalyst was soluble in $[D_6]$benzene at high temperatures. By the use of the lithium cation as catalyst, the transmetallation was expected not to take place because the formation of $Ar_4Sb\bullet ArLi\bullet TFPB^-$ would be a high energy process. The activity of these catalysts was examined by heating $[D_6]$benzene solutions (or suspensions) of Tol_5Sb (**1**) or Ar_5Sb (**6**) with or without the catalysts in sealed NMR tubes at 165 °C and the results are shown in Table 6. The LCR from **1** and **6** were dramatically accelerated by $Cu(acac)_2$, with the reaction being completed within 5 min at 165 °C. However, for **2**-**5**, $Cu(acac)_2$ was found to cause more of the LER (ca. 20%) as a side reaction than LiTFPB.

This result may have come from the contribution of transmetallation of the aryl group to copper, and moreover, there is the possibility of biaryl formation from arylcopper species generated by transmetallation. Therefore, we chose LiTFPB as the catalyst to avoid complexity.

<Table 6>

The catalyzed LCR by LiTFPB was applied for mixed pentaarylantimony compounds (**2**–**5**). Experimental ratios of biaryls and triarylantimony compounds were determined by GC and relative integral intensities in ^{19}F NMR. As shown in Table 7, bitolyl (Tol-Tol) was not formed at all from Ar_2Tol_3Sb (**3**), Ar_3Tol_2Sb (**4**), or Ar_4TolSb (**5**). Although bitolyl was obtained in the LCR from $ArTol_4Sb$ (**2**), we believe that bitolyl should be formed from Tol_5Sb (**1**) since we already found that the rate of LE from **2** was exceptionally fast. The percentages of LER shown in the last column of Table 7 were calculated from the yields of the Sb^{III} compounds. For example, in the case of the

LCR of Ar_2Tol_3Sb (**3**), 6% of Ar_2TolSb, which should be a product from LC after LE (Ar_3Tol_2Sb (**4**)), was formed. The percentage of LER could be estimated to be at least 12% because an equal quantity (6%) of $ArTol_4Sb$ (**2**) should be formed together with Ar_3Tol_2Sb (**4**). Since $ArTol_2Sb$ should also be formed from Ar_2Tol_3Sb (**3**), the real percentage of LE must be higher than the calculated value (12% in this case). The LCR of $ArTol_4Sb$ (**2**) gave Ar-Ar in 10% yield, which could not be formed directly from **2**. Therefore, there is a large experimental uncertainty in the LER percentage for **2**.

<Table 7>

The catalytic effect of the Li^+ cation can be rationalized by assuming coordination of the cations with (i) the fluorine atom in the CF_3 group, (ii) the benzene ring of the tolyl and/or the aryl group, or (iii) the eletron-rich apical Sb-C bond. Since high catalytic acitvity was observed for Tol_5Sb (**1**) compared with Ar_5Sb (**6**) (see Table 6), the coordination of the

Li^+ cation to the benzene ring of the tolyl group, or the eletron-rich apical Sb-C bond should be the likely reason for the catalytic effect. However, the effect of the cation does not seem to affect the pathway of the LCR because the ratio of the biaryls formed in the catalyzed reaction in solution were very close to those of FVT (vide infra) although LER took place competitively throughout the LCR in the catalytic system in solution.

Flash vacuum thermolysis (FVT) of $Ar_nTol_{5-n}Sb$: As described in the previous section, the LER could still be competitive in a certain extent with the catalytic LCR from each of $Ar_nTol_{5-n}Sb$. Therefore, in order to obtain conclusive results for the selectivity in the LCR from only one specified species, we chose LCR in vapor phase as a promising solution, in which collision of molecules (causing LER) would be negligible. We investigated a variety of experimental conditions for the flash vacuum thermolysis (FVT) using laser irradiated sublimation of a solid compound and injection of a sample solution to the oven with a syringe etc, and finally found satisfactory conditions. The equipment is shown in Figure 8. A solid sample was vaporized by preheating (125 ˚C) under vacuum (2×10^{-3} Torr) and introduction to the oven (300 ˚C) for LCR. Details on the experimental procedures are described in the Experimental section. The experimental ratios of the biaryls were found to be essentially independent of oven temperatures between 200 and 300 °C (Table 8).

<Figure 8>

<Table 8>

The results of FVT are shown in Table 9 with the yields of mixed biaryls together with statistically expected ratios. Although the yields of mixed triarylantimony(III) compounds, generated from the LCR, essentially corresponded to the yields of Ar-Ar and Ar-Tol for each starting material, a small extent of protonolysis to give Tol-H and Ar-H was found to take place competitively, which may have resulted from contact to the surface of the filling. Protonolysis is essentially independent of the LCR and should not influence the experimental ratios of biaryls. $ArTol_4Sb$ is again an exception, from which Ar-Ar (19%) and Tol-Tol (14%) were obtained probably after very fast LER (2 $ArTol_4Sb \rightarrow Tol_5Sb + Ar_2Tol_3Sb$). Tol-Tol was not detected at all from Ar_4TolSb (**5**), Ar_3Tol_2Sb (**4**), or Ar_2Tol_3Sb (**3**). The results are very similar to those of the catalyzed LCR (Table 7), which shows that LER is only a minor process during LiTFPB catalyzed LCR.

<Table 9>

The fact that Tol-Tol could not be detected at all from Ar_4TolSb (**5**), Ar_3Tol_2Sb (**4**), or Ar_2Tol_3Sb (**3**) rules out the possibility of LCR taking place via equatorial-equatorial coupling, because **3** and **4** would be expected to give Tol-Tol if the equatorial-equatorial coupling were actually operative. Apical-equatorial coupling certainly may not be the case because **3** and **4** would be expected to give rise to small but definite amounts of Tol-Tol from a somewhat less stable stereoisomer which should be present to a certain extent by BPR. There is an apparent trend for the more electronegative *p*-$CF_3C_6H_4$ group to preferrentially participate in the LCR to afford Ar-Ar and Ar-Tol. Based on the quantitative yield of Ar-Ar and Ar-Tol in Table 9, it is concluded that the relative rate of LCR to give Ar-Tol is faster than that of Ar-Ar. This is consistent with the result in Table 6. Therefore, these experimental results on the LCR from mixed pentaarylantimony compounds can only be interpreted by invoking the idea that apical-apical coupling is the sole reaction path. That is, once the apical substituents start a bending motion for the LCR, the pairing is maintained through the transition state on to the final products with the conservation of the momentum, i.e., we propose to call this a "***memory effect***". The memory effect is intuitively acceptable because the hypervalent bond (apical bond: 3c-4e) is weak and polarized (polarizable), and is thus more liable to undergo bending motion than equatorial sp^2 bonds. Mechanism of the apical-apical LCR is illustrated in Scheme 13, using Ar_2Tol_3Sb (**3**) as an example.

<Scheme 13>

Moreover, the preference for the more electronegative substituents, which probably occupy the apical sites, to participate in the LCR seems to be general. As previously reported by us (see Table 1),[18] the LCR from triarylbis(phenylethynyl)antimony(V) compounds showed that no biaryls were formed and that the more electronegative the aryl group became, the more PhC≡C-Ar was obtained along with the decrease of PhC≡C-C≡CPh.

Recent advanced ab initio calculations predicted that the LCR from SbH_5 underwent in a manner of equatorial-equatorial coupling through transition state **C** as shown in Figure 9.[11] The charge distribution in **C** was shown to have the electron density of the leaving dihydrogens in the equatorial positions be less than that of other hydrogens. The apparent contradiction between theoretical studies and the present experimental results regarding which set of sites combine to form the biaryls, may be due in part to the neglection of 2p-orbitals of the aryl group by using hydrogens in the place of carbons in the calculation.

In regards with our proposed mechanism involving a memory effect, Carpenter has stated that reacting molecules or reacting positions in a molecule tend to take a trajectory from reactants, through the intermediate, and on to the product that is closest to a straight-line pathway, where conservation of momentum plays an important role.[37] Further theoretical studies are necessary to make clear what are the essential reasons for the present contradiction.

<Figure 9>

Conclusion

In conclusion, we have successfully prepared every possible pentaarylantimony compound of $Ar_nTol_{5-n}Sb$ (Ar = *p*-$CF_3C_6H_4$, Tol = *p*-$CH_3C_6H_4$) composition and have determined their structures in the solid state and in solution. As for the solid state, X-ray crystallographic analyses revealed that all the newly prepared compounds **2**-**6** bear trigonal bipyramidal (TBP) geometry. In all the cases, the electron-withdrawing Ar group(s) occupied the apical position(s), which was consistent with the general understanding on the apicophilicity concept. In solution, pseudorotation of all the compounds appeared to be fast, and the process could not be frozen on the NMR time scale. The intrinsic ^{13}C chemical shifts for the ipso carbon atoms in the apical (δ_{ap} 161.3 for Ar and 155.5 for Tol) and the equatorial (δ_{eq} 140.7 for Ar and 135.5 for Tol) positions were estimated based on variable temperature ^{13}C NMR study.

The ligand exchange reaction (LER) was found to take place upon heating a mixed pentaaryantimony at 60 °C in solution instead of the ligand coupling reaction (LCR). By statistical analysis for the LER, the relative stability constant (S_i) was calculated for each compound, showing Ar_2Tol_3Sb (**3**) to be the most stable compound in the LER equilibrium. The LER can be regarded as a reaction unique to hypervalent compounds, being consistent with the nature of hypervalent bonding.

The ligand coupling reaction (LCR) was found to take place easily in solution by the use of LiTFPB as the catalyst, and no bitolyl (Tol-Tol) formation was observed except in the case of $ArTol_4Sb$ (**2**), which shows very fast LER. Conclusive results on the selectivity of the LCR were obtained from experiments using flash vacuum thermolysis (FVT). The results were essentially the same as those with the catalytic LCR in solution, and the conclusion was obtained that apical-apical coupling was the sole process of LCR for pentaarylantimony compounds.

Experimental Section

General: ^1H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using a JEOL EX-400 spectrometer. ^1H NMR (90 MHz) and ^{19}F NMR (85 MHz) spectra were also routinely recorded using a Hitachi R-90H spectrometer. Chemical shifts are reported (δ scale) from internal tetramethylsilane for ^1H and ^{13}C or from external fluorotrichloromethane for ^{19}F. All the synthetic procedures are provided in the Supporting Information.

X-ray crystallography. Details of X-ray crystallographic analysis are provided in the Supporting Information. CCDC-613263 (**2**), 613264 (**3**), 613265 (**4**), 613266 (**5**) and 613267 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Flash vacuum thermolysis (FVT) of 2, 3, 4 and 5. The apparatus for FVT is shown in Figure 8. A pure mixed pentaarylantimony compound (10-15 mg) is placed at the head of a quartz tube in which "fillings" are packed in the center. "Fillings" are crushed quartz glass pretreated with "coating" to avoid protonolysis and any catalyzed reaction on the surface of the fillings. "Coating" means that the fillings are boiled in a benzene solution of a mixture of Ar_5Sb, Tol_5Sb, Ar_3Sb, Tol_3Sb, Tol_2 and etc. overnight and the fillings are washed out thoroughly with acetone and de-ionized water and dried. The residual compounds were not detected at all by heating the quartz tube with the filling up to 300 °C for several hours at high vacuum (10^{-5} Torr). The FVT tube was evacuated first to $1\text{-}2 \times 10^{-5}$ Torr with an oil diffusion pump and the pressure was kept at $1\text{-}2 \times 10^{-3}$ Torr under a gentle and constant stream of argon throughout the pyrolysis. A solid sample was heated up to 120-125 °C by a ribbon heater ("preheating") at the head of the quartz tube, and the sublimed sample was pyrolyzed in the oven (300 °C) to give coupled products and triarylantimony, which were trapped by liquid N_2. The reaction period was 30 min and the obtained products were analyzed by GC. About 5-10% of the starting material was sublimed into the oven, and the residual sample which did not vaporize was analyzed by NMR in order to estimate the extent of LER. Under these conditions, the extent of LER was determined to be less than 5% except for $ArTol_4Sb$, in which the rate of LER was exceptionally fast. FVT experiments were carried out at least four times for all of the compounds (except for $ArTol_4Sb$) and the data is given as the average of all of the runs and are presented with probable errors (see Table 9). The data for $ArTol_4Sb$ is an average of two runs.

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References

[1] K.-y. Akiba, *Chemistry of Hypervalent Compounds*, Wiley-VCH, New York, **1999**.

[2] a) R. R. Holmes, *Pentacoordinated Phosphorus–Structure and Spectroscopy*; ACS Monograph 175, 176, Vol. I, II, American Chemical Society, Washington, DC, **1980**; b) D. E. C. Corbridge, *Phosphorus: An Outline of Its Chemistry, Biochemistry, and Technology*, 4th ed., Elsevier, Amsterdam, **1990**, Chapter 14,

pp. 1233–1256; c) R. Burgada, R. Setton, in *The Chemistry of Organophosphorus Compounds*, Vol. 3 (Ed.: F. R. Hartley), Wiley-Interscience, Chichester, **1994**, pp. 185-272; d) *Handbook of Organophosphorus Chemistry* (Ed.: R. Engel), Marcel Dekker, New York, **1992**; e) S. Matsukawa, S. Kojima, K. Kajiyama, Y. Yamamoto, K.-y. Akiba, S. Re, S. Nagase, *J. Am. Chem. Soc.* **2002**, *124*, 13154-13170.

[3] a) M. Nakamoto, S. Kojima, S. Matsukawa, Y. Yamamoto, K.-y. Akiba, *J. Organometal. Chem.* **2002**, *643-644*, 441-452; b) S. Matsukawa, K. Kajiyama, S. Kojima, S.-y. Furuta, Y. Yamamoto, K.-y. Akiba, *Angew. Chem.* **2002**, *114*, 4912-4916; *Angew. Chem. Int. Ed.* **2002**, *41*, 4718-4722; c) S. Trippett, *Phosphorus Sulfur* **1976**, *1*, 89-98; d) S. Trippett, *Pure and Appl. Chem.* **1970**, *40*, 595-604; e) G. Buono, J. R. Llinas, *J. Am. Chem. Soc.* **1981**, *103*, 4532-4540; f) M. Eisenhut, H. L. Mitchell, D. D. Traficante, R. J. Kaufman, J. M. Deutsch, G. M. Whitesides, *J. Am. Chem. Soc.* **1974**, *96*, 5385-5397; g) C. G. Moreland, G. O. Doak, L. B. Littlefield, N. S. Walker, J. W. Gilje, R. W. Braun, A. H. Cowley, *J. Am. Chem. Soc.*

1976, *98*, 2161-2165; h) L. V. Griend, R. G. Cavell, *Inorg. Chem.* **1983**, *22*, 1817-1820; i) S. Kumaraswamy, C. Muthiah, K. C. Kumara Swamy, *J. Am. Chem. Soc.* **2000**, *122*, 964-965; j) P. Kommana, S. Kumaraswamy, J. J. Vittal, K. C. Kumara Swamy, *Inorg. Chem.* **2002**, *41*, 2356-2363.

[4] a) R. Hoffmann, J. M. Howell, E. L. Muetterties, *J. Am. Chem. Soc.* **1972**, *94*, 3047-3058; b) R. S. McDowell, A. Streitwieser Jr., *J. Am. Chem. Soc.* **1985**, *107*, 5849-5855; c) J. A. Deiters, R. R. Holmes, J. M. Holmes, *J. Am. Chem. Soc.* **1988**, *110*, 7672-7681; d) P. Wang, Y. Zhang, R. Glaser, A. E. Reed, P. v. R. Schleyer, A. Streitwieser, Jr., *J. Am. Chem. Soc.* **1991**, *113*, 55-64; e) H. Wasada, K. Hirao, *J. Am. Chem. Soc.* **1992**, *114*, 16-27; f) G. R. J. Thatcher, A. S. Campbell, *J. Org. Chem.* **1993**, *58*, 2272-2281; g) P. Wang, Y. Zhang, R. Glaser, A. Streitwieser, P. v. R. Schleyer, *J. Comput. Chem.* **1993**, *14*, 522-529; h) B. D. Wladkowski, M. Krauss, W. J. Stevens, *J. Phys. Chem.* **1995**, *99*, 4490-4500; i) J. C. Martin, *Science* **1983**, *221*, 509-514.

[5] R. S. Berry, *J. Chem. Phys.* **1960**, *32*, 933-938. The energy

of pseudorotation, that is, the mutual positional exchange of a pair of apical ligands with a pair of equatorial ligands in acyclic compounds, such as PH_5 was calculated as ca. 2-3 kcal mol^{-1} (see ref 11), corresponding to a rapid process, in contrast to tetracoordinate phosphorus species that are ordinarily stereochemically rigid except when substitutions at the phosphorus atom facilitate an edge-inversion process (D. A. Dixon, A. J. Arduengo, III, T. Fukunaga, *J. Am. Chem. Soc.* **1986**, *108*, 2461-2462; D. A. Dixon, A. J. Arduengo, III, *J. Phys. Chem.* **1987**, *91*, 3195-3200; D. A. Dixon, A. J. Arduengo, III, *J. Am. Chem. Soc.* **1987**, *109*, 338-341).

[6] a) K.-y. Akiba, H. Fujikawa, Y. Sunaguchi, Y. Yamamoto, *J. Am. Chem. Soc.*, **1987**, *109*, 1245-1247; b) Y. Yamamoto, H. Fujikawa, H. Fujishima, K.-y. Akiba, *J. Am. Chem. Soc.*, **1989**, *111*, 2276-2283; c) K.-y. Akiba, H. Nakata, Y. Yamamoto, S. Kojima, *Chem. Lett.*, **1992**, 1559-1562; d) Y. Yamamoto, X. Chen, S. Kojima, K. Ohdoi, M. Kitano, Y. Doi, K.-y. Akiba, *J. Am. Chem. Soc.*, **1995**, *117*, 3922-3932; e) K.-y. Akiba, H. Fujishima, A. Ohtani, S. Kojima, Y. Yamamoto, *Bull. Soc. Chim. Belg.*,

1997, *106*, 577-584; f) Y. Yamamoto, S. Kojima, H. Fujishima, H. Fujikawa, K.-y. Akiba, *Bull. Soc. Chim. Belg.*, **1997**, *106*, 651-657; g) K. Toyota, Y. Yamamoto, K.-y. Akiba, *Chem. Lett.*, **1999**, 783-784; h) K. Toyota, Y. Wakisaka, Y. Yamamoto, K.-y. Akiba, *Organometallics*, **2000**, *19*, 5122-5133; i) K. Toyota, Y. Yamamoto, K.-y. Akiba, *Organometallics*, **2000**, *19*, 5134-5142; j) M. Takahashi, A. Ishiguro, M. Maeda, M. Takeda, K. Toyota, Y. Yamamoto, K.-y. Akiba, *Z. Naturforsch. Teil. A.*, **2002**, *57a*, 631-639. For reviews, see k) K.-y. Akiba, Y. Yamamoto, *The Chemistry of Organic Arsenic, Antimony, and Bismuth Compounds* (Ed.: S. Patai), John Wiley & Sons, Chichester, **1994**, p. 761; l) *Gmelin Handbook of Inorganic Chemistry. Organoantimony Compounds* (Ed.: M. Wieber), Springer-Verlag, Berlin, **1982**, part 3; m) D. Hellwinkel, *Top. Curr. Chem.* **1983**, *109*, 1-63.

[7] The *N*-X-*L* designation was proposed previously: X, central atom; *N*, formal valence shell electrons about an X; *L*, the number of ligands. C. W. Perkins, J. C. Martin, A. J. Arduengo III., A. Algeria, J. K. Kochi, *J. Am. Chem. Soc.*, **1980**, *102*,

7753-7759.

[8] J. M. Howell. *J. Am. Chem. Soc.* **1977**, *99*, 7447-7452.

[9] W. Kutzelnigg, J. Wasilewski. *J. Am. Chem. Soc.* **1982**, *104*, 953-960.

[10] J. Moc, A. E. Dorigo, K. Morokuma, *Chem. Phys. Lett.* **1993**, *204*, 65-72.

[11] J. Moc, K. Morokuma, *J. Am. Chem. Soc.* **1995**, *117*, 11790-11797.

[12] P. Kolandaivel, R. Kumaresan, *J. Mol. Struct.* **1995**, *337*, 225-229.

[13] D. Hellwinkel, W. Lindner, *Chem. Ber.* **1976**, *109*, 1497-1505.

[14] a) S. A. Glover, *J. Chem. Soc., Perkin Trans. 1* **1980**, 1338-1344; b) D. H. R. Barton, S. A. Glover, S. V. Ley, *J. Chem. Soc., Chem. Commun.,* **1977**, 266-267.

[15] a) T. Kawai, N. Furukawa, S. Oae, *J. Chem. Soc., Perkin Trans. II*, **1987**, 405-411; b) S. Oae, Y. Uchida, *Acc. Chem. Res.* **1991**, *24*, 202-208.

[16] T. Kawashima, F. Ohno, R. Okazaki, H. Ikeda, S. Inagaki, *J. Am. Chem. Soc.* **1996**, *118*, 12455-12456.

[17] a) Y. Uchiyama, N. Kano, T. Kawashima, *J. Am. Chem. Soc.* **2003**, *125*, 13346-13347; b) *Idem. J. Org. Chem.* **2006**, *71*, 659-670.

[18] K.-y. Akiba, T. Okinaka, M. Nakatani, Y. Yamamoto, *Tetrahedron Lett.* **1987**, *28*, 3367-3368.

[19] K. Shen, W. E. McEwen, A. P. Wolf, *J. Am. Chem. Soc.* **1969**, *91*, 1283-1288.

[20] C. Brabant, J. Hubert, A. L. Beauchamp, *Can. J. Chem.* **1973**, *51*, 2952-2957.

[21] B. Raynier, B. Maegell, R. Commandeur, H. Mathais, *Nouv. J. Chim.* **1979**, *3*, 393-401.

[22] T. B. Brill, G. G. Long, *Inorg. Chem.* **1972**, *11*, 225-228.

[23] a) K. Seppelt, in *Heteroatom Chemistry* (Ed.: E. Block), VCH Verlagsgesell schaft, Weinheim, Germany, **1990**, p. 335; b) A. Schmuck, D. Leopold, K. Seppelt, *Chem. Ber.* **1989**, *122*, 803-808; c) A. Schmuck, P. Pyykkoe, K. Seppelt, *Angew. Chem.* **1990**, *102*, 211-213; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 213-215; d) A. Schmuck, D. Leopold, S. Wallenhauer, K. Seppelt, *Chem. Ber.* **1990**, *123*, 761-766.

[24] G. Doleshall, N. A. Nesmeyanov, A. Reutov, *J. Organomet. Chem.* **1971**, *30*, 369-375.

[25] L. N. Markovskij, V. E. Pashinnik, A. V. Kirsanov, *Synthesis* **1973**, 787-789.

[26] G. Wittig, K. Clauss, *Liebigs Ann. Chem.* **1952**, 577, 26-39.

[27] H. J. Frohn, H. Maurer, *J. Fluorine Chem.* **1986**, *34*, 129-145.

[28] M. Nunn, D. B. Sowerby, D. M. Wesolek, *J. Organomet. Chem.* **1983**, *251*, C45-C46.

[29] a) P. J. Wheatley, G. Wittig, *Proc. Chem. Soc. (London)*, **1962**, 251-252; b) P. J. Wheatley, *J. Chem. Soc.*, **1964**, 2206-2222; c) C. P. Brock, D. F. Webster, *Acta Cryst. B*, **1976**, *32*, 2089-2094; d) P. J. Wheatley, *J. Chem. Soc.*, **1964**, 3718-3723.

[30] A. C. Beauchamp, M. J. Bennett, F. A. Cotton, *J. Am. Chem. Soc.*, **1968**, *90*, 6675-6680.

[31] C. Brabant, B. Blanck, A. C. Beauchamp, *J. Organomet. Chem.* **1974**, *82*, 231-234.

[32] a) A. C. Hengge, *Acc. Chem. Res.* **2002**, *35*, 105-112, and references therein; b) S. D. Lahiri, G. Zhang, D.

Dunaway-Mariano, K. N. Allen, *Science* **2003**, *299*, 2067-2071; c) R. R. Holmes, *Acc. Chem. Res.* **2004**, *37*, 746-753.

[33] H. J. Reich, N. H. Phillips, *J. Am. Chem. Soc.* **1986**, *108*, 2102-2103.

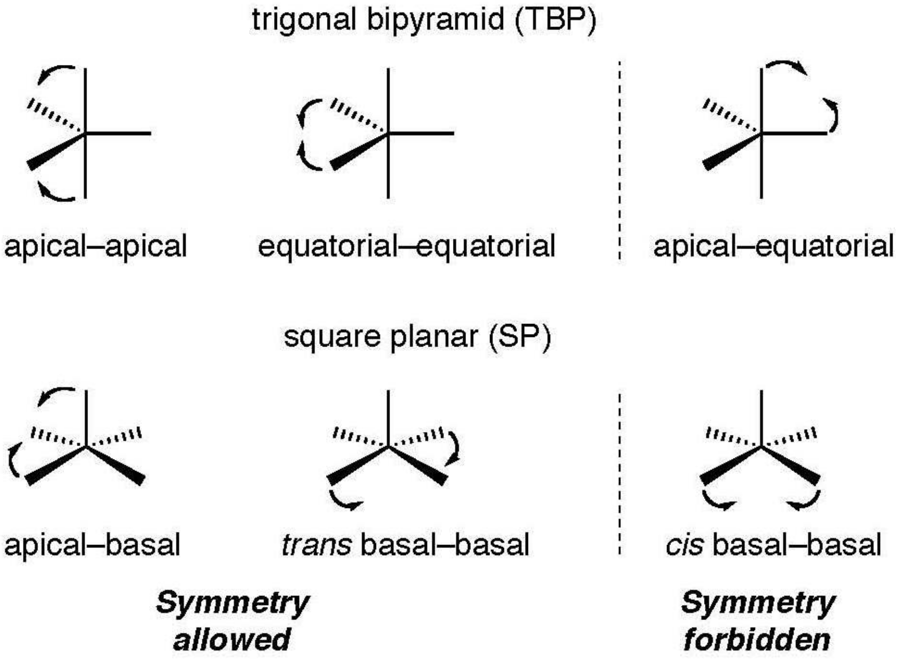
[34] for the LER of triarylantimony dihalides, see a) E. L. Muetterties, W. Mahler, K. J. Packer, R. Schmutzler, *Inorg. Chem.* **1964**, *3*, 1298-1303; b) C. G. Moreland, M. H. O'Brien, C. E. Douthit, G. G. Long, *Inorg. Chem.* **1968**, *7*, 834-836; c) S. N. Bhattacharya, M. Singh, *Indian J. Chem., A.* **1978**, *16*, 778-781.

[35] V. A. Dodonov, O. P. Bolotova, A. V. Gushchin, *J. Gen. Chem. USSR (engl. Transl.)*, **1988**, *58*, 629-630.

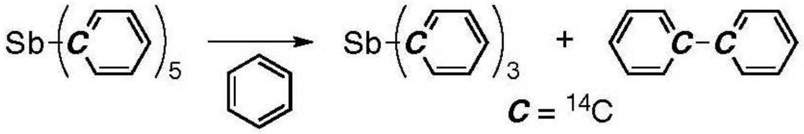
[36] K. Fujiki, S.-y. Ikeda, H. Kobayashi, A. Mori, A. Nagira, J. Nie, T. Sonoda, Y. Yagupolskii, *Chem. Lett.* **2000**, 62-63.

[37] a) B. K. Carpenter, *J. Am. Chem. Soc.* **1985**, *107*, 5730-5732; b) B. A. Lyons, J. Pfeifer, B. K. Carpenter, *J. Am. Chem. Soc.* **1991**, *113*, 9006-9007.

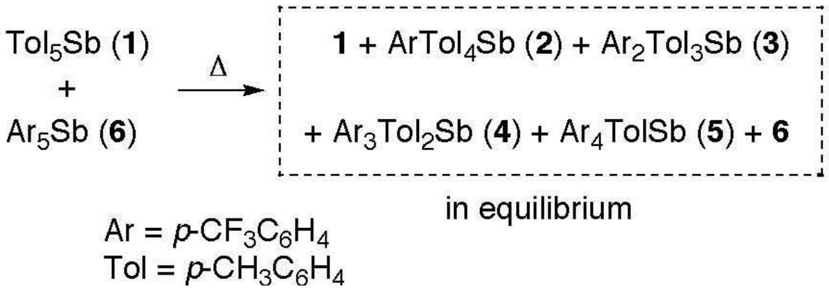
Scheme and Figure Legends



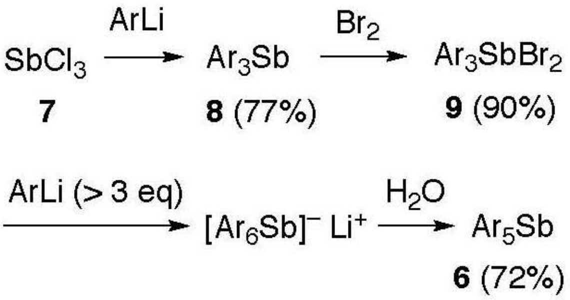
Scheme 1. Theoretically proposed reaction modes for LCR.



Scheme 2. LCR of ^{14}C-labelled pentaphenylantimony.[19]

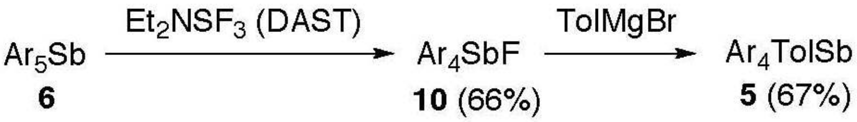


Scheme 3. Ligand scrambling by the ligand exchange reaction (LER).

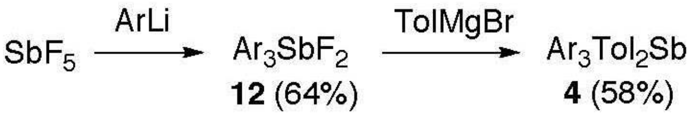


Scheme 4. Preparation of Ar_5Sb (**6**).

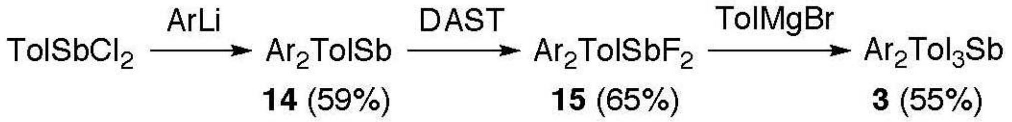
Scheme 5. Ligand exchange reaction via hexacoordinate antimony ate complex.



Scheme 6. Preparation of Ar_4TolSb (**5**).

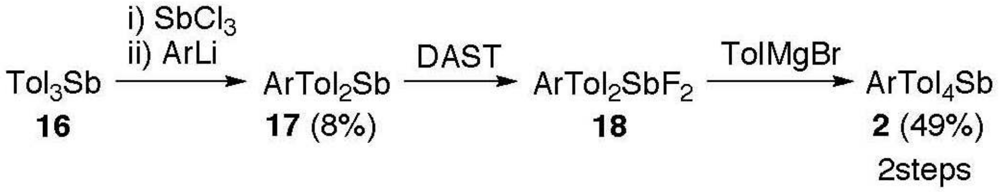


Scheme 7. Preparation of Ar_3Tol_2Sb (**4**).



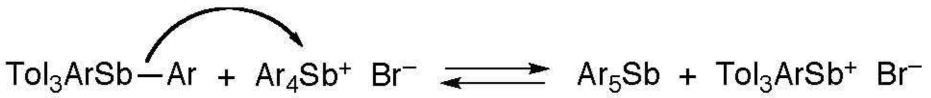
$$\mathrm{TolSbCl_2} \xrightarrow{\mathrm{ArLi}} \underset{\mathbf{14}\ (59\%)}{\mathrm{Ar_2TolSb}} \xrightarrow{\mathrm{DAST}} \underset{\mathbf{15}\ (65\%)}{\mathrm{Ar_2TolSbF_2}} \xrightarrow{\mathrm{TolMgBr}} \underset{\mathbf{3}\ (55\%)}{\mathrm{Ar_2Tol_3Sb}}$$

Scheme 8. Preparation of Ar_2Tol_3Sb (**3**).



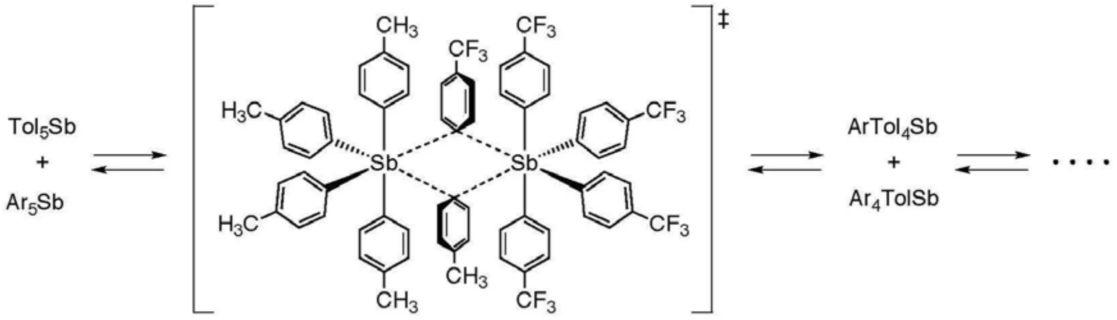
$$\underset{\mathbf{16}}{\mathrm{Tol_3Sb}} \xrightarrow[\text{ii) ArLi}]{\text{i) SbCl}_3} \underset{\mathbf{17}\ (8\%)}{\mathrm{ArTol_2Sb}} \xrightarrow{\mathrm{DAST}} \underset{\mathbf{18}}{\mathrm{ArTol_2SbF_2}} \xrightarrow{\mathrm{TolMgBr}} \underset{\mathbf{2}\ (49\%)\ \text{2steps}}{\mathrm{ArTol_4Sb}}$$

Scheme 9. Preparation of $ArTol_4Sb$ (**2**).



$$\mathrm{Tol_3ArSb{-}Ar} + \mathrm{Ar_4Sb^+\ Br^-} \rightleftharpoons \mathrm{Ar_5Sb} + \mathrm{Tol_3ArSb^+\ Br^-}$$

Scheme 10. Halogenoantimony-assisted disproportionation.



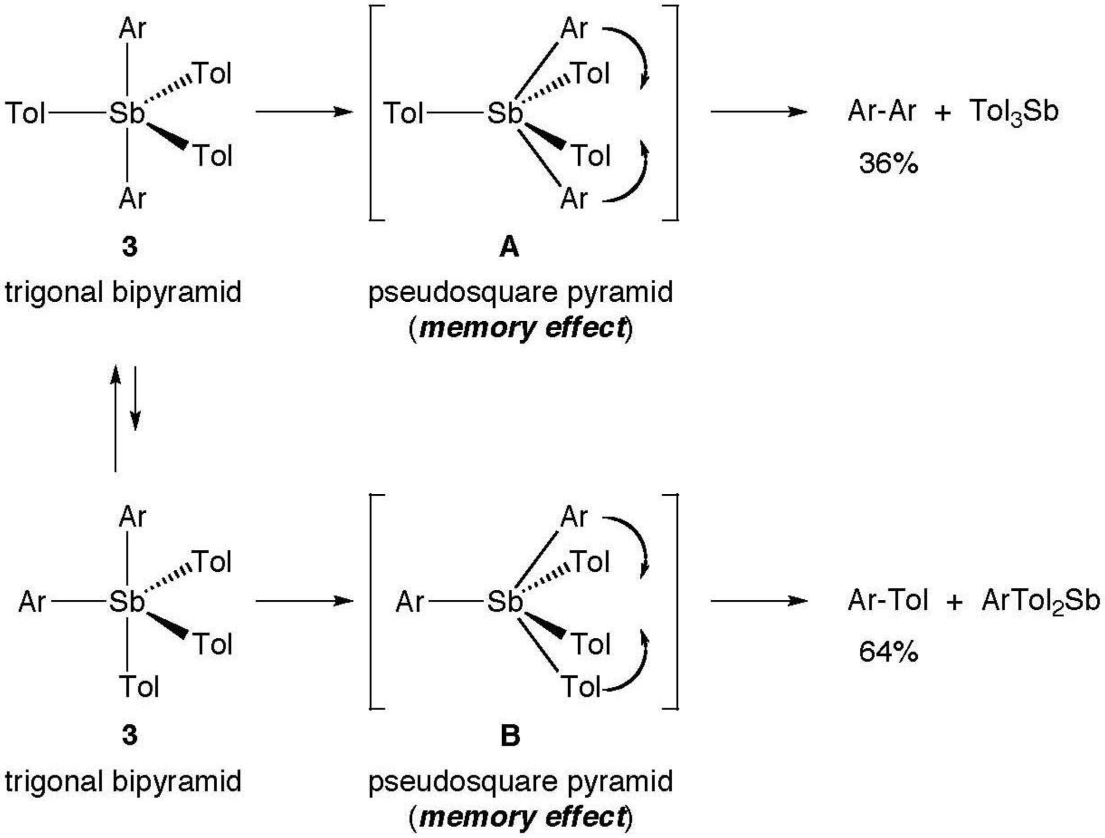
Scheme 11. Proposed mechanism for the ligand exchange reaction.

$$\underset{\mathbf{1}}{\mathrm{Tol_5Sb}} + \mathrm{Ar'_5Sb} \longrightarrow \textit{ligand scrambling}$$

$$\longrightarrow \mathrm{Tol\text{-}Tol + Tol\text{-}Ar' + Ar'\text{-}Ar'}$$

$$\mathrm{Ar'} = \mathrm{Ph},\ p\text{-}\mathrm{ClC_6H_4},\ p\text{-}\mathrm{CF_3C_6H_4}$$

Scheme 12. LCR from equilibrated mixtures.



Scheme 13. Mechanism for the apical-apical LCR of pentaarylantimony compounds.

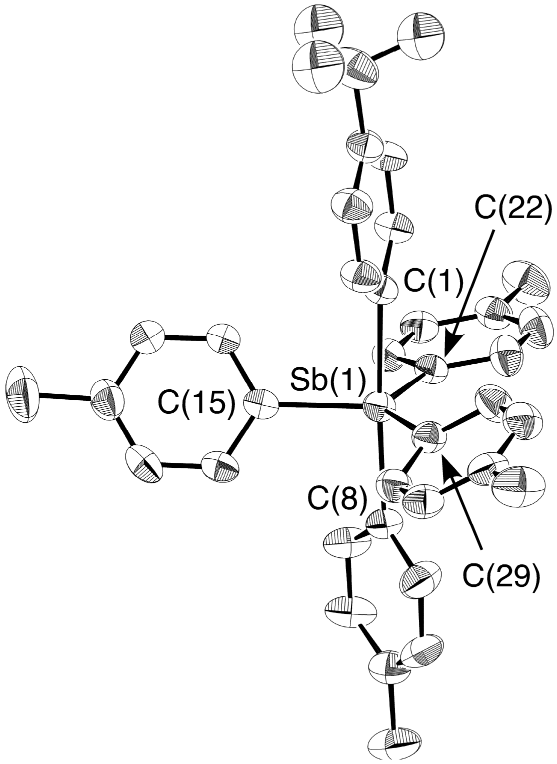


Figure 1. The ORTEP drawing of $ArTol_4Sb$ (**2**) showing the thermal ellipsoids at the 30% probability level. The hydrogen atoms are omitted for clarity.

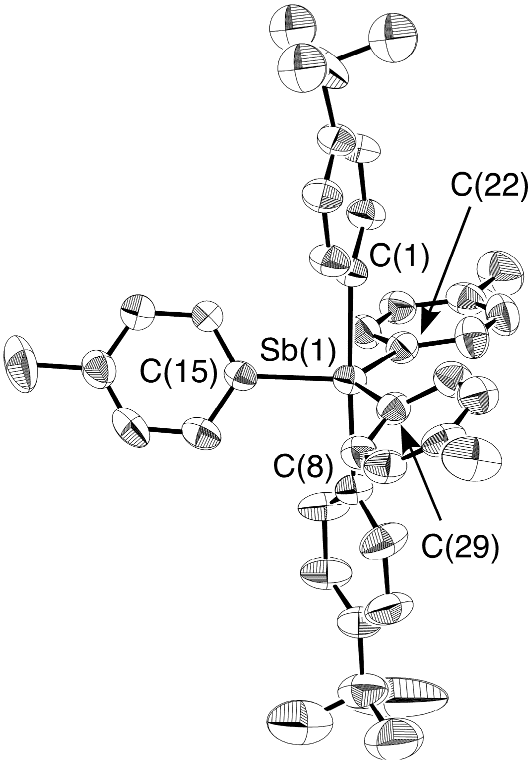


Figure 2. The ORTEP drawing of Ar_2Tol_3Sb (**3**) showing the thermal ellipsoids at the 30% probability level. The hydrogen atoms are omitted for clarity.

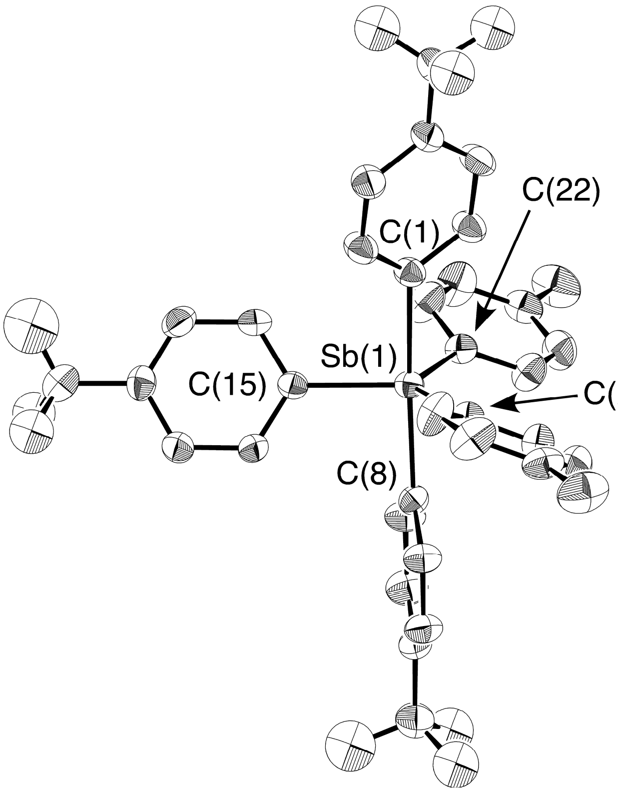


Figure 3. The ORTEP drawing of Ar_3Tol_2Sb (**4**) • 0.5 Et_2O showing the thermal ellipsoids at the 30% probability level. The hydrogen atoms and the Et_2O molecule are omitted for clarity.

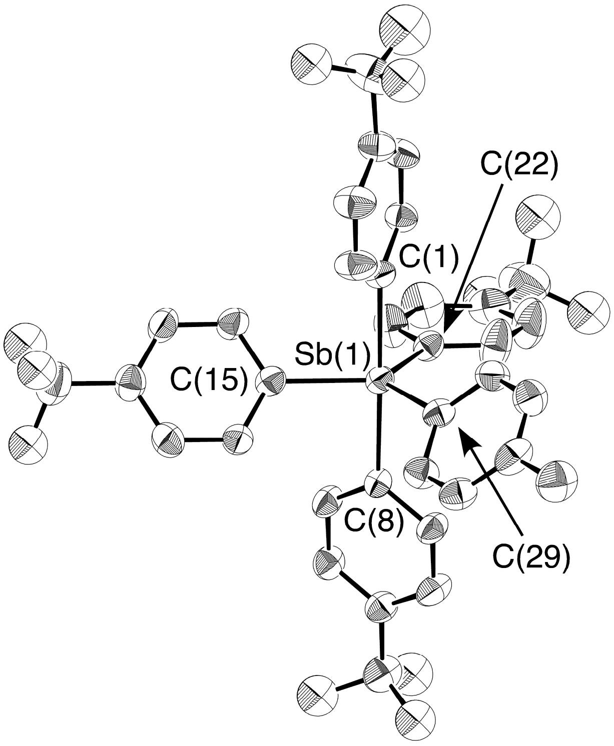


Figure 4. The ORTEP drawing of Ar_4TolSb (**5**) • 2.5 C_6H_6 showing the thermal ellipsoids at the 30% probability level. The hydrogen atoms and the benzene molecules are omitted for clarity.

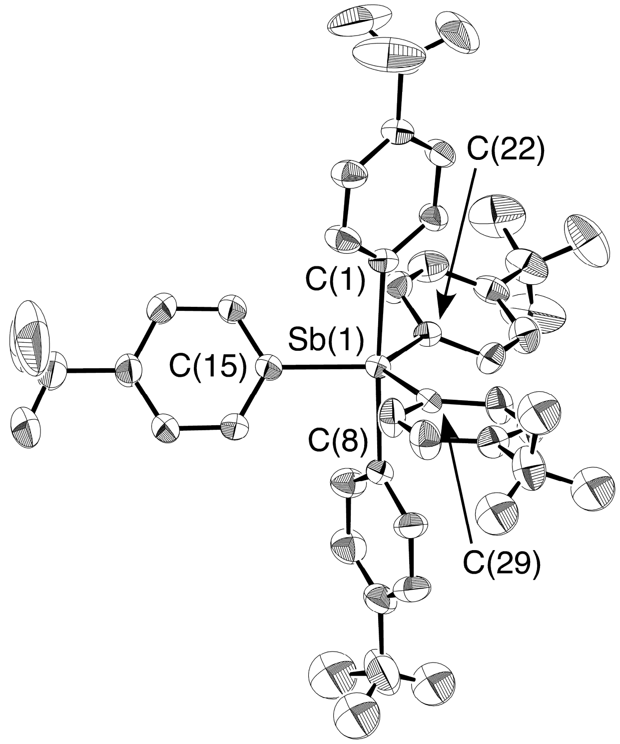


Figure 5. The ORTEP drawing of Ar_5Sb (**6**) showing the thermal ellipsoids at the 30% probability level. One of the two independent molecules is shown. The hydrogen atoms are omitted for clarity.

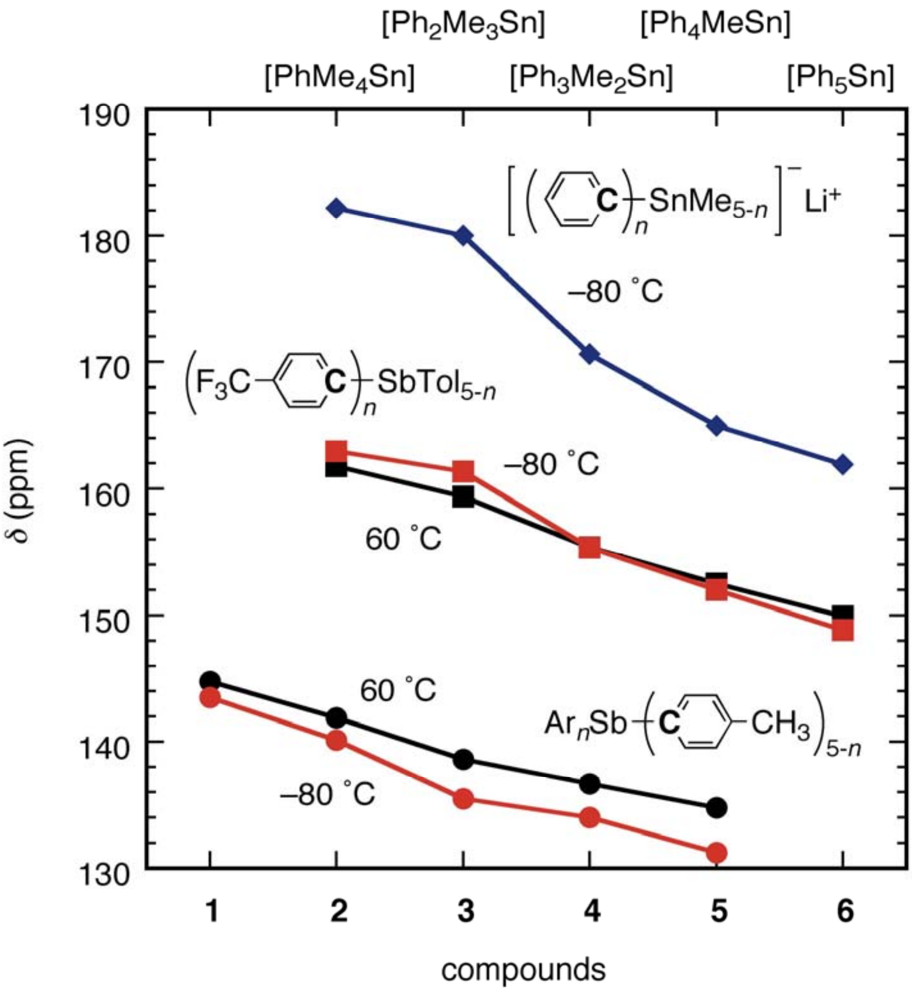


Figure 6. ^{13}C NMR chemical shifts for the ipso carbon of Ar groups. Blue diamonds: Reich's tin ate complexes at –80 ˚C,[33] red squares: Ar ipso carbons of **2**–**6** at –80 ˚C, black squares: Ar ipso carbons of **2**–**6** at 60 ˚C, red circles: Tol ipso carbons of **1**–**5** at –80 ˚C, black circles: Tol ipso carbons of **1**–**5** at 60 ˚C.

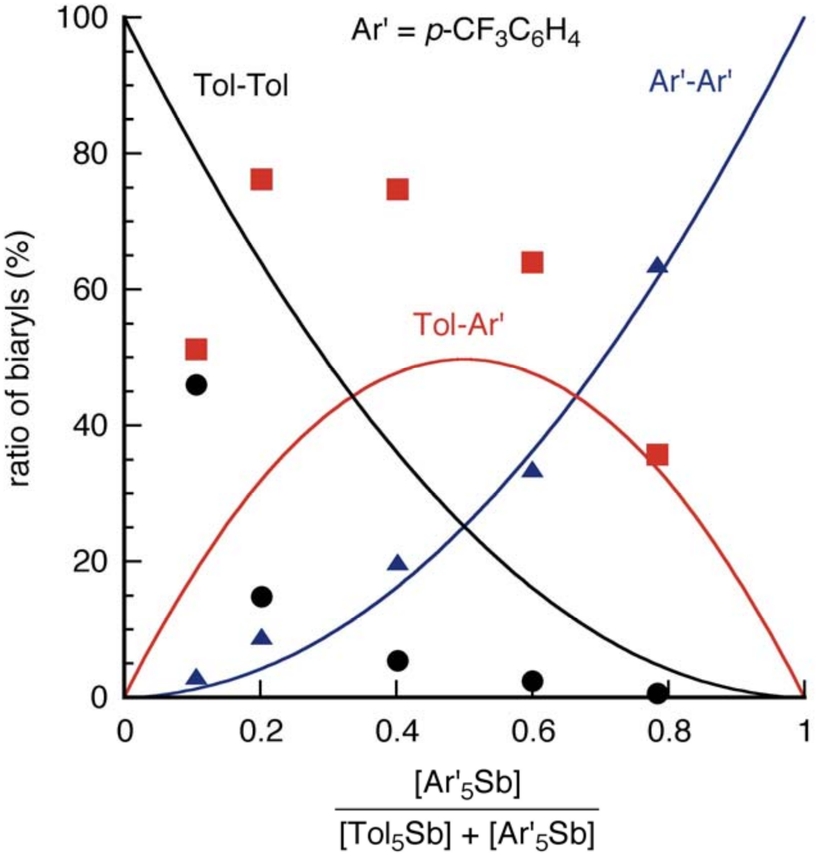


Figure 7. Distribution of biaryls generated from the LCR using a mixture of **1** and **6**. Circles (black), squares (red), and triangles (blue): experimental ratio of Tol-Tol, Tol-Ar', and Ar'-Ar', respectively. Solid lines: calculated statistical ratios.

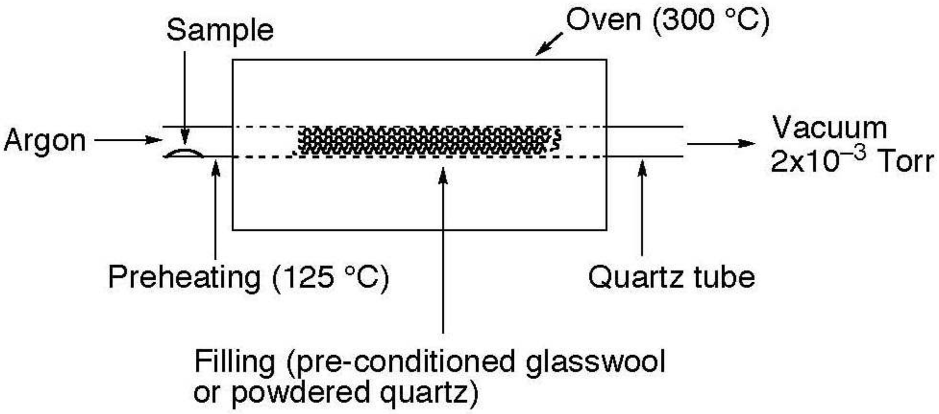


Figure 8. Apparatus of flash vacuum thermolysis (FVT)

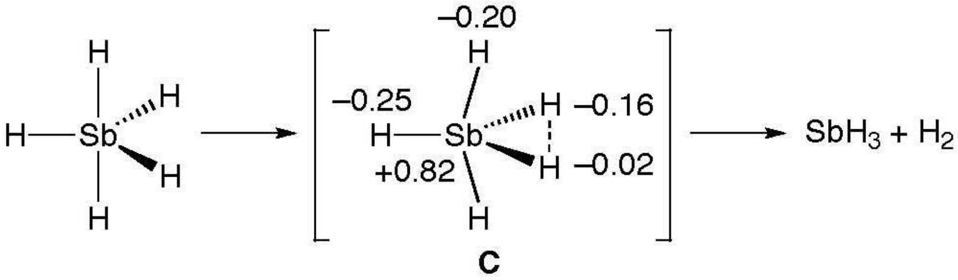


Figure 9. The reaction mode of LCR predicted by theoretical calculations.[11]

Tables

Table 1. LCR of bis(phenylethynyl)triarylantimony.[18]

<Figure for Table 1>

	Yield (%)		
Aryl	PhC≡C-C≡CPh	PhC≡C-Ar	Ar-Ar
p-$CH_3C_6H_4$	76	24	0
C_6H_5	66	34	0
p-ClC_6H_4	50	50	0

Table 2. Reaction conditions and yields of the mixed pentaarylantimony compounds **2**–**5**.[a]

entry	halogenide	metalloorganic reagent	reaction time	product (yield)	purity[f]
1[b]	Ar_4SbF	TolMgBr	15 min	**5** (67%)	>98%
2[c]	Ar_3SbF_2	TolMgBr	20 min	**4** (58%)	>98%
3[d]	$Ar_2TolSbF_2$	TolMgBr	20 min	**3** (55%)	>98%
4[e]	$ArTol_2SbF_2$	TolMgBr	20 min	**2** (49%)	>98%
5	Tol_4SbF	ArMgBr	25 min	**2** (–)	–
6	Tol_4SbF	ArMgBr	25 min	**2** (16%)[g]	~90%
7	Tol_4SbF	ArMgBr	25 min	**2** (30%)[h]	~80%
8	Ar_3SbBr_2	TolMgBr	15 min	**4** (30%)	>98%

[a] All reactions were performed at 0 °C. [b] Scheme 6. [c] Scheme 7. [d] Scheme 8. [e] Scheme 9. [f] based on ^{19}F NMR. [g] A THF-ether mixture was used. [h] A DME-ether mixture was used.

Table 3. Selected bond parameters of the crystal structures of **1**–**6**.

	1[a]	**2**	**3**	**4**	**5**	**6** (1st)[d]	**6** (2nd)[d]
				Bond Lengths (Å)			
Sb–C(1)	2.238(17)	2.263(4)[b]	2.256(6)[b]	2.239(6)[b]	2.241(5)[b]	2.240(7)[b]	2.237(7)[b]
Sb–C(8)	2.254(14)	2.246(5)	2.252(7)[b]	2.245(6)[b]	2.234(6)[b]	2.241(7)[b]	2.230(7)[b]
Sb–C(15)	2.145(12)	2.136(5)	2.155(7)	2.140(6)[b]	2.154(6)[b]	2.149(7)[b]	2.151(7)[b]
Sb–C(22)	2.151(15)	2.148(4)	2.139(6)	2.135(6)	2.154(6)[b]	2.146(7)[b]	2.157(7)[b]
Sb–C(29)	2.180(14)	2.154(4)	2.142(7)	2.150(6)	2.142(6)	2.155(7)[b]	2.130(7)[b]
				Bond Angles (deg)			
C(1)–Sb–C(8)	178.0(6)	176.95(17)	176.4(2)	175.6(2)	177.06(18)	176.3(3)	175.5(3)
C(1)–Sb–C(15)	90.4(6)	90.28(17)	86.1(3)	91.6(2)	88.7(2)	92.4(3)	91.1(3)
C(1)–Sb–C(22)	90.9(7)	89.27(17)	90.2(2)	92.0(2)	91.4(2)	90.2(3)	91.5(3)
C(1)–Sb–C(29)	91.0(7)	86.52(17)	90.7(3)	86.6(2)	89.6(2)	88.1(2)	87.3(3)
C(8)–Sb–C(15)	91.5(6)	92.65(18)	90.6(3)	90.9(2)	90.7(2)	91.2(3)	93.3(3)
C(8)–Sb–C(22)	88.2(7)	90.39(18)	92.7(3)	90.3(2)	86.4(2)	87.7(3)	86.5(3)
C(8)–Sb–C(29)	88.3(7)	91.35(18)	90.2(3)	89.0(2)	93.3(2)	90.6(3)	90.7(3)
C(15)–Sb–C(22)	116.0(7)	113.11(17)	118.3(3)	114.1(2)	121.7(2)	119.1(3)	114.8(3)
C(15)–Sb–C(29)	114.0(7)	117.54(18)	127.8(3)	122.8(2)	117.4(2)	115.7(3)	120.1(3)
C(22)–Sb–C(29)	130.0(7)	129.16(17)	113.8(2)	123.2(2)	120.9(2)	125.2(2)	125.1(3)
D[c]	48.0	47.8	48.6	52.4	55.4	51.1	50.4

[a] ref 20. [b] Sb–C(Ar) bond. [c] ref 23. [d] Two independent molecules.

Table 4. Equilibrium ratio resulted from a mixture of Tol_5Sb (**1**) and Ar_5Sb (**6**) (t/a = 2.74), and the relative stability constants for **1**–**6**.

Tol_5Sb (**1**) : $ArTol_4Sb$ (**2**) : Ar_2Tol_3Sb (**3**) : Ar_3Tol_2Sb (**4**) : Ar_4TolSb (**5**) : Ar_5Sb (**6**)

$$\approx t^5S_0 : 5t^4aS_1 : 10t^3a^2S_2 : 10t^2a^3S_3 : 5ta^4S_4 : a^5S_5$$

	1	**2**	**3**	**4**	**5**	**6**
statistical ratio	0.753	1.373	1.00	0.367	0.0667	0.00467
observed ratio	0.590	0.835	1.00	0.193	0.0275	0.00413
S_i [a]	0.780	0.608	1.00	0.526	0.410	0.846

[a] Relative stability constant (i = 0-5)

Table 5. Relative stability constants (S_i) from various t/a ratios.

entry	t/a	**1**	**2**	**3**	**4**	**5**	**6**
1	0.46	—	—	1.0	0.68	0.46	0.46
2	0.64	—	—	1.0	0.66	0.47	0.65
3	0.99	0.15	0.42	1.0	0.93	0.50	0.11
4[a]	1.50	0.41	0.53	1.0	0.66	0.31	0.28
5	1.70	0.58	0.62	1.0	0.77	0.38	0.42
6	2.74	0.78	0.61	1.0	0.53	0.41	(0.85)
S_i (av.)[b]		0.48±0.27	0.54±0.09	1.0	0.71±0.13	0.42±0.07	0.38±0.20

[a] from Ar_2Tol_3Sb (**3**). [b] Relative stability constant (i = 0-5).

Table 6. Conversion percentage (%) of the LCR from **1** and **6** after 30 min at 165 °C.

catalyst	Tol_5Sb (**1**)	Ar_5Sb (**6**)
none	23	no reaction after 19 h
LiTFPB	91	16
$Cu(acac)_2$	100	100

Table 7. LCR catalyzed by LiTFPB [TFPB: B(3,5-$(CF_3)_2C_6H_3)_4$].[a]

	molar ratio	statistical ratio			experimental ratio			
compound	cat./sample	Ar-Ar	Ar-Tol	Tol-Tol	Ar-Ar	Ar-Tol	Tol-Tol	LER (%)
Ar_4TolSb (**5**)[b]	0.11	60	40	0	73	27	0	–
Ar_3Tol_2Sb (**4**)[c]	0.20	30	60	10	51	49	0	–
Ar_3Tol_2Sb (**4**)[c]	0.088	30	60	10	50	50	0	>12
Ar_2Tol_3Sb (**3**)[c]	0.10	10	60	30	31	69	0	>12
Ar_2Tol_3Sb (**3**)[c]	0.13	10	60	30	32	68	0	>15
$ArTol_4Sb$ (**2**)[c]	0.089	0	40	60	10	76	14	>24

[a] Reaction condition: in C_6D_6 at 165 °C. Concentration of the sample: 0.011-0.034 M. [b] Reaction time = 3.5 h. [c] Reaction time = 10 min.

Table 8. Temperature effect on the FVT from Ar_3Tol_2Sb (**4**).

oven temp. (K)	Ar-Ar	Ar-Tol	Tol-Tol
300	58 ± 1.9	42 ± 1.9	0
250	59	41	0
200	61	39	0
statistical ratio	30	60	10

Table 9. Yields of biaryls by flash vacuum thermolysis.

	statistical ratio			experimental ratio		
compound	Ar-Ar	Ar-Tol	Tol-Tol	Ar-Ar	Ar-Tol	Tol-Tol
Ar_4TolSb (**5**)	60	40	0	76 ± 2.3	24 ± 2.3	0
Ar_3Tol_2Sb (**4**)	30	60	10	58 ± 1.9	42 ± 1.9	0
Ar_2Tol_3Sb (**3**)	10	60	30	36 ± 1.5	64 ± 1.5	0
$ArTol_4Sb$ (**2**)	0	40	60	19	67	14

Text for the Table of Contents

Apical-apical ligand coupling of pentaarylantimony: All the possible combinations of the pentaarylantimony compounds ($Ar_nTol_{5-n}Sb$; Ar = *p*-$CF_3C_6H_4$, Tol = *p*-$CH_3C_6H_4$) **1-6** (*n* = 0-5) were synthesized and fully characterized by means of NMR spectroscopies and X-ray crystallography. Ligand exchange reactions (LERs) of these compounds underwent easily in solution to cause ligand scrambling. Investigations on the selectivity of ligand coupling reaction (LCR) of **3**-**5** by use of flash vacuum thermolysis led to the conclusion that apical-apical coupling is the sole process of LCR (*memory effect*).

<Figure for TOC>

Keywords: Antimony; Hypervalent compounds; Ligand coupling reaction; Ligand exchange reaction; X-ray analysis