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

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Abstract: All possible combinations of mixed pentaarylantimony compounds bearing *p*-methylphenyl and *p*-trifluoromethylphenyl groups were synthesized; $Ar_nTol_{5-n}Sb$ (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 feature trigonal-bipyramidal (TBP) geometry with the more electronegative *p*-trifluoromethylphenyl substituents selectively occupying the apical positions. Consideration of the chemical shifts of the ipso carbons of the aryl and tolyl groups suggested that the solution structures of **1–6** were also TBP, although their pseudorotation could not be frozen even at −80 °C. Ligand-exchange reactions (LERs) took place between **1** and **6** at ≈60 °C in [D$_6$]benzene and all 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) of **2–5** in solution were greatly accelerated by adding $Cu(acac)_2$ or Li^+ $TFPB^-$ (TFPB: $[3,5\text{-}(CF_3)_2C_6H_3]_4B$), whereby the rate becomes comparable to the LER. The use of flash vacuum thermolysis (FVT) allowed the LCR to occur with very little ligand-exchange; the exception $ArTol_4Sb$ had very fast ligand-exchange. The selectivities of the LCRs were calculated from the yield of the biaryls synthesized by using FVT. These results were highly consistent with reactions catalyzed in solution, in which bitolyl was not obtained at all. The experimental results suggested that the LCR of pentaarylantimony compounds proceeds in the manner of apical–apical coupling.

Keywords: antimony · hypervalent compounds · ligand effects · ligand-coupling · structure elucidation

Introduction

Hypervalent compounds of group 15 elements have been extensively investigated in terms of structure, permutational behavior, and reactions.[1] Pentacoordinate phosphorus chemistry especially, has unveiled important properties of hypervalent compounds.[2] Notable basic properties among them are apicophilicity[3,4] and pseudorotation.[5a] 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 (BPR).[5a] Relative to phosphorus chemistry, hypervalent antimony chemistry has been less studied,[1,6] therefore, clarification of its fundamental properties is of interest.

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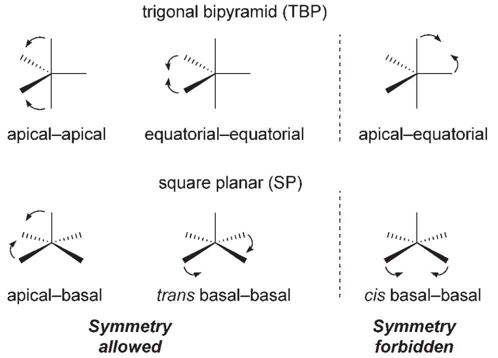
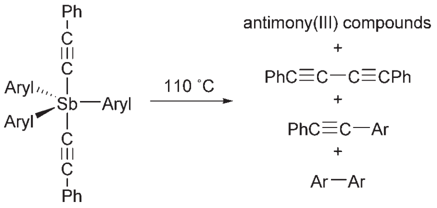
The ligand-coupling reaction (LCR) is one of the fundamental reactions of hypervalent organic molecules of main group elements. Selectivity in the LCR of 10-M-5[7] (M: group 15 elements) compounds has attracted interest in relation to their bonding arrangement, which differs greatly in compounds of ordinary valency, such as tetravalent compounds. Tetravalent compounds usually hold sp^3 or sp^2 hybrid orbitals and, therefore, show no distinction in the nature of the bonds concerning coupling reactions. However, for 10-M-5 compounds for which there are two possible geometries, TBP and square pyramidal (SP), there are usually two kinds of bonds; two apical and three equatorial bonds in the TBP and one axial and four basal bonds in the SP.[6] Theoretical investigation of 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 LCR between the apical–equatorial ligands was forbidden (Scheme 1). The symmetry-forbidden apical–equatorial-coupling process has been reported once to be favored,[8] whereas recent calculations support the conclusion by Hoffmann that equatorial–equatorial coupling is the lowest energy process for PH_5, AsH_5, and SbH_5,[9–12] although BiH_5 favors the apical–equatorial process.[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 the 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 experimentally the selectivity of the LCR should fulfil the following requirements: 1) the LCR should take place in a concerted manner, 2) the reverse reactions from the products should not take place, 3) the system should be sterically unbiased, 4) the structure of the starting compounds should be unambiguous (preferably determined by X-ray analysis).



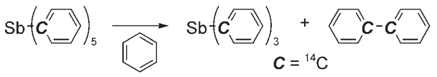
Scheme 1. Theoretically proposed reaction modes for LCR.

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



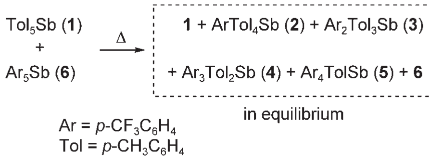
Aryl	Yield [%] PhC≡C–C≡CPh	PhC≡C–Ar	Ar–Ar
p-$CH_3C_6H_4$	76	24	0
C_6H_5	66	34	0
p-ClC_6H_4	50	50	0

Pioneering work by McEwen showed that the LCR of ^{14}C-labeled pentaphenylantimony in unlabeled benzene afforded biphenyl bearing ^{14}C labels on both phenyl rings and ^{14}C-labeled triphenylantimony.[19] Neither ^{14}C-labeled benzene nor biphenyl, bearing only one ^{14}C label for the two phenyl rings, was formed. Therefore, the LCR was confirmed to take place concertedly (Scheme 2). Mixed pentaarylantimony compounds that have different carbon substituents, which are electronically different but sterically similar, would be good candidates for the examination of the LCR as 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, $Ar_nTol_{5-n}Sb$ ($n = 1$–4: Ar = p-$CF_3C_6H_4$, Tol = p-$CH_3C_6H_4$).



Scheme 2. Ligand-coupling reaction (LCR) of ^{14}C-labeled pentaphenylantimony.[19]

Here, we report on the syntheses and the structural determination of a series of mixed pentaarylantimony compounds, $Ar_nTol_{5-n}Sb$ ($n = 0$–5) **1**–**6**. Structures in the solid state were determined by X-ray crystallographic analyses and those in solution were established by ^{13}C NMR spectroscopy. TBP structures are suggested for all cases. The ligand-exchange reaction (LER) 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 ob-

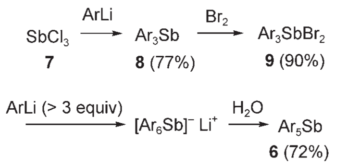


Scheme 3. Ligand scrambling by the ligand-exchange reaction (LER).

serving their molar ratios in an appropriate mixture of **1** and **6** in benzene (60 °C). In equilibrium, Ar_2Tol_3Sb (**3**) was the most stable compound among these species. Finally, selectivities of the ligand-coupling reaction (LCR) of each of **2**–**5**, catalyzed by LiTFPB (TFPB = $[3,5\text{-}(CF_3)_2C_6H_3]_4B$) in solution as well as those obtained by flash vacuum thermolysis (FVT), are presented and the mechanism of LCR will be discussed.

Results and Discussion

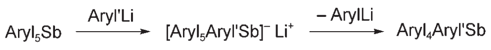
Preparation of Tol_5Sb (1), $ArTol_4Sb$ (2), Ar_2Tol_3Sb (3), Ar_3Tol_2Sb (4), Ar_4TolSb (5), and Ar_5Sb (6) (Ar = *p*-$CF_3C_6H_4$, Tol = *p*-$CH_3C_6H_4$): The preparation of pentakis(*p*-methylphenyl)antimony (**1**) has already been reported.[20,21] Pentakis(*p*-trifluoromethylphenyl)antimony (**6**) was prepared as shown in Scheme 4. Stibine Ar_3Sb (**8**) was prepared



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

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 two equivalents of ArLi gave Ar_5Sb (**6**). However, to obtain "super pure" **6**, it was necessary to use an excess amount of ArLi to form the ate complex $[Ar_6Sb]^-Li^+$. 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 a similar procedure by using $[Tol_6Sb]^-Li^+$.

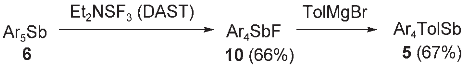
The synthesis of the mixed compounds **2**–**5** was more difficult and required laborious operations. For mixed pentaarylbismuth compounds, Seppelt[23] reported a synthesis that used triarylbismuth dihalides and aryllithium as the starting materials. We tried to apply this method to the preparation 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 for this is the general ability of pentaarylantimony compounds to readily form ate complexes (Scheme 5). Consequently, the desired pentaarylantimony compounds form ate complexes with the excess organolithium reagents and then 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 on the formation of the desired pentaarylantimony.



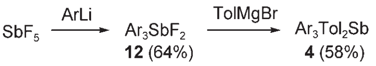
Scheme 5. LER by the hexacoordinate antimony ate complex.

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 (see below). 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 chosen for the synthesis of **2**–**5**. Ar_4SbF (**10**) is readily 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 even easier. In an attempt to prepare Ar_5Sb (**6**) directly from antimony pentafluoride (**11**) with seven equivalents 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).

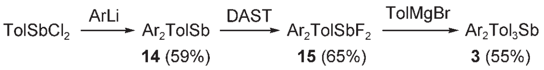


Scheme 6. Preparation of Ar_4TolSb (**5**).



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

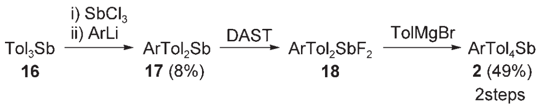
The preparation of the mixed fluorides $Ar_2TolSbF_2$ (**15**) and $ArTol_2SbF_2$ (**18**) was less facile. First, Ar_2TolSb (**14**) was prepared by the reaction of ArLi with $TolSbCl_2$ (Scheme 8).



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

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 due to contamination by 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).

ArTol$_4$Sb (**2**) was prepared in essentially the same way. The preparation of Tol$_2$SbCl from Tol$_3$Sb (**16**) and SbCl$_3$ (**7**) was tried repeatedly according to procedures described for Ph$_2$SbCl.[28] However, we found that a large amount of by-products such as TolSbCl$_2$ and Tol$_3$SbCl$_2$ were always formed, so we were not able to isolate Tol$_2$SbCl in pure form by recrystallization, although various solvents were examined. Consequently, we arylated the crude reaction mixture with ArLi, then separated crude ArTol$_2$Sb (**17**) by preparative HPLC. Recrystallization of the separated product from methanol gave pure ArTol$_2$Sb (**17**), although in a low yield (8%). Fluorination was again achieved with DAST to give **18** as a yellowish oil, which was used in the following arylation to give the desired product **2** in 49% yield (Scheme 9).



Scheme 9. Preparation of ArTol$_4$Sb (**2**).

The desired pentaarylantimony(V) compounds **2**–**5** were successfully prepared in good yields by the use of TolMgBr (Schemes 6–9, and entries 1–4 in Table 2). However, the reaction conditions had to be controlled carefully to avoid the redistribution reaction shown in Scheme 5. 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 times caused the ligand-exchange reaction. If prepared pure, the mixed pentaarylantimony compounds are thermally stable and behave like usual homoleptic pentaarylantimony compounds. However special care is necessary in handling ArTol$_4$Sb (**2**) as it is very sensitive to the LER and the reaction even continues (ca. 5%) during recrystallization (dry benzene in the refrigerator over several days). Notably, the melting points of **2**–**5** depend very much on the speed of heating because the LER takes place during the measurements.

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

Entry	Halogenide	Metalloorganic reagent	Reaction time	Product (yield)	Purity[b]
1[c]	Ar$_4$SbF	TolMgBr	15 min	**5** (67%)	>98%
2[d]	Ar$_3$SbF$_2$	TolMgBr	20 min	**4** (58%)	>98%
3[e]	Ar$_2$TolSbF$_2$	TolMgBr	20 min	**3** (55%)	>98%
4[f]	ArTol$_2$SbF$_2$	TolMgBr	20 min	**2** (49%)	>98%
5	Tol$_4$SbF	ArMgBr	25 min	**2** (–)	–
6	Tol$_4$SbF	ArMgBr	25 min	**2** (16%)[g]	≈90%
7	Tol$_4$SbF	ArMgBr	25 min	**2** (30%)[h]	≈80%
8	Ar$_3$SbBr$_2$	TolMgBr	15 min	**4** (20%)	≈90%

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

Attempts to prepare ArTol$_4$Sb (**2**) by using ArMgBr and Tol$_4$SbF resulted in an impure product (entries 5–7 in Table 2). It is 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. This is evident by comparison of entries 2 and 8 in Table 2, the fluoride clearly 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 therefore, nucleophilic attack on the antimony atom by Grignard reagents is accelerated.

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 a SP geometry.[23] Antimony compounds seem to be a borderline case, as shown in the well-known SP structure of Ph$_5$Sb[30] and the TBP structures of Tol$_5$Sb[20] and Ph$_5$Sb•0.5 C$_6$H$_{12}$.[31] In addition, the influence of the para substituents on the apicophilicity of 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 in depth. Therefore, investigation of the X-ray structures of the mixed pentaarylantimony compounds is of 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 that was 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 ($D = 0$–15° SP; $D =$ 45–60° TBP).[23] All the determined structures clearly assume a TBP structure similar to **1**.[20] Two independent molecules were observed for **6**. The apical positions in **2**–**5** are selectively occupied by the Ar groups. It can be concluded that the apicophilicity of the Ar group is higher than that of the Tol group, as predicted.

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 to avoid steric hindrance. The apical bonds were also of similar length to each other [C(1) and C(8)] (2.23–2.26 Å), and they

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 [°]			
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.

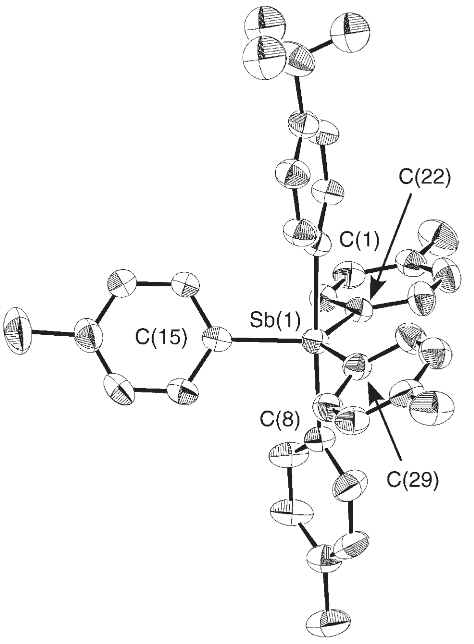


Figure 1. ORTEP drawing of ArTol$_4$Sb (**2**) showing the thermal ellipsoids at the 30 % probability level. The hydrogen atoms are omitted for clarity.

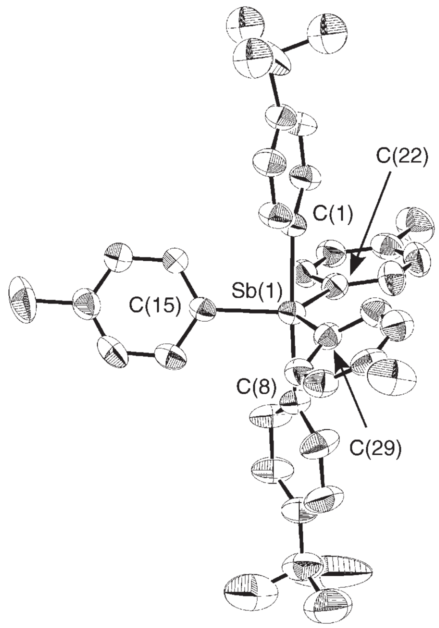


Figure 2. ORTEP drawing of Ar$_2$Tol$_3$Sb (**3**) showing the thermal ellipsoids at the 30 % probability level. The hydrogen atoms are omitted for clarity.

were slightly longer (by ≈0.10 Å) than the equatorial bonds. No significant differences between the Sb−C(Ar) and Sb−C(Tol) bond lengths were observed, even though the electronic properties of Ar and Tol groups are different. Bond angles conform to the essential character of TBP structure.

The measured structures **2**–**6** have D angles between 47.8 and 55.4°, which indicates 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 similar TBP structure with $D=48°$,[20] the structure of Ph$_5$Sb ($D=14.8°$)[30] has clearly shown the possibility for some pentaarylantimony compounds to adopt the SP structure. The preference for 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 adopt a TBP structure. However, this trend was not rigidly held for all of the compounds and was also dependent on the nature of the central elements, as exemplified by Ph$_5$Bi ($D=13°$) and Tol$_5$Bi ($D=35°$).[23] It is possible that the bulkiness of the methyl and trifluoromethyl groups in comparison with hydrogen cause changes in the lattice energies and make the TBP structure

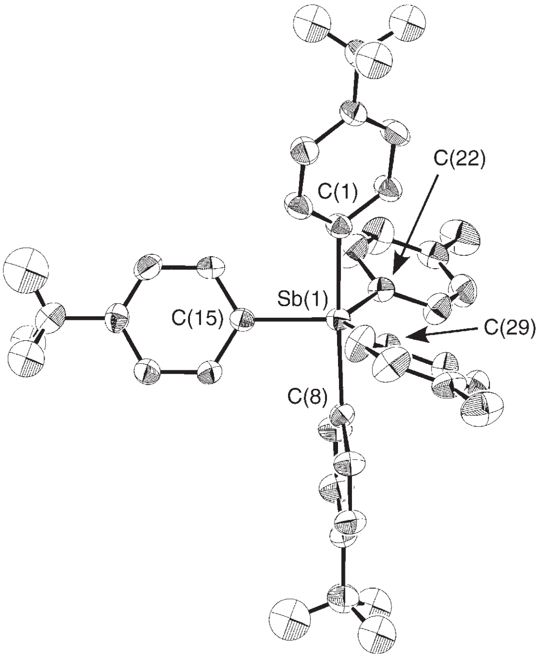


Figure 3. ORTEP drawing of Ar_3Tol_2Sb (**4**)$\cdot$0.5 Et_2O showing the thermal ellipsoids at the 30% probability level. The hydrogen atoms and the Et_2O molecule are omitted for clarity.

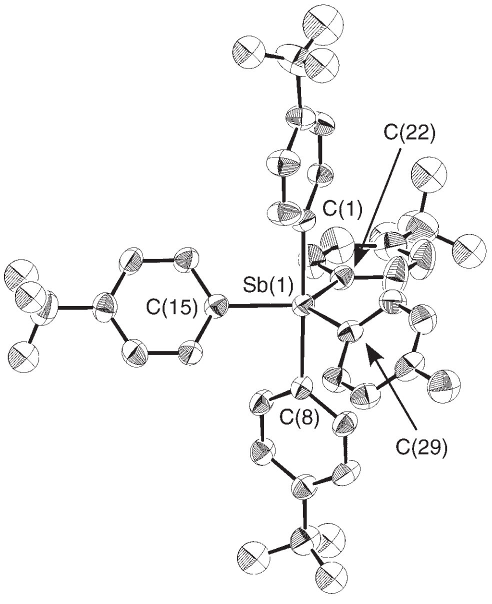


Figure 4. ORTEP drawing of Ar_4TolSb (**5**)$\cdot$2.5 C_6H_6 showing the thermal ellipsoids at the 30% probability level. The hydrogen atoms and the benzene molecules are omitted for clarity.

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. For the compounds bearing multiple Ar groups

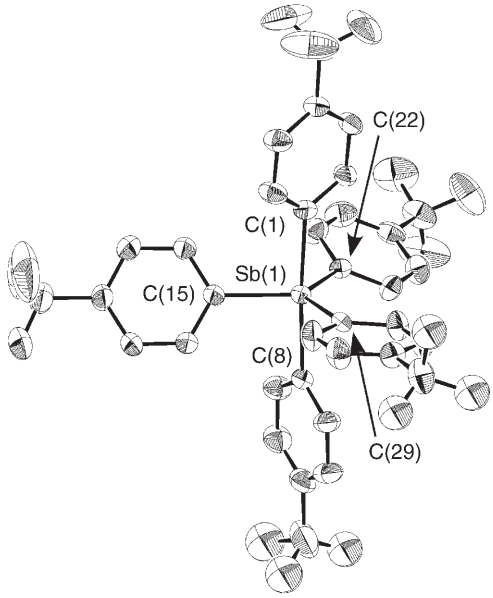


Figure 5. ORTEP drawing of Ar_5Sb (**6**) showing the thermal ellipsoids at the 30% probability level. One of the two independent molecules is shown. The hydrogen atoms are omitted for clarity.

(**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 spectroscopy.

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 to resolve a structure in solution that was otherwise difficult to determine. Pentacoordinate main-group-element compounds are highly flexible due to rapid Berry pseudorotation (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 alongside 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 ($\delta = 162.9$ ppm in **2**, 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 occupy mainly 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,

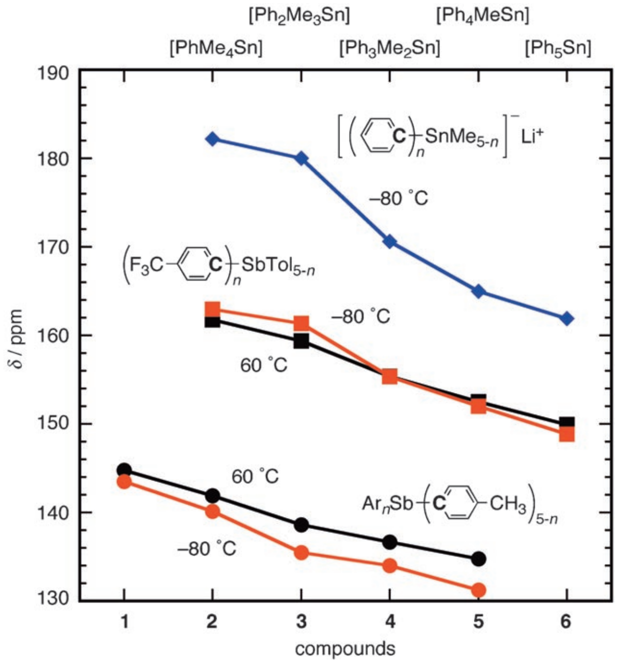


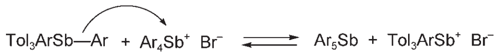
Figure 6. ^{13}C NMR chemical shifts for the ipso carbon of the Ar groups. ◆ Reich's tin ate complexes at −80 °C,[33] ■ Ar ipso carbons of **2**–**6** at −80 °C, ■ Ar ipso carbons of **2**–**6** at 60 °C, ● Tol ipso carbons of **1**–**5** at −80 °C, ● Tol ipso carbons of **1**–**5** at 60 °C.

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**.

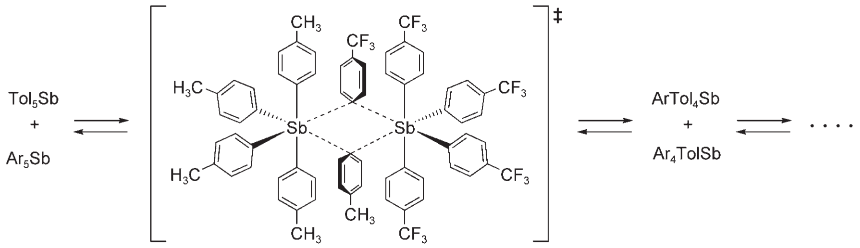
The averaged $^{13}C_{ipso}$ chemical shift of the Ar group can be calculated to be $\delta_{Ar} = (a\delta_{ap} + e\delta_{eq})/(a + e)$, in which δ_{ap} (=161.3 ppm) and δ_{eq} are intrinsic chemical shifts of the Ar groups at the apical and equatorial positions, respectively, and a is the number of Ar ligands in the apical positions, and e is the number in the equatorial positions. In **6**, all positions are occupied by the Ar groups, the averaged chemical shift (δ_{Ar}) of the ipso carbon ($\delta = 148.9$ ppm) should be equal to $(2\delta_{ap} + 3\delta_{eq})/5$. 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 carbons of **4** and **5** are calculated to be 154.4 ppm $[(2\delta_{ap} + \delta_{eq})/3]$ and 151.0 ppm $[(2\delta_{ap} + 2\delta_{eq})/4]$, respectively, which are consistent with the observed values for **4** and **5** (155.3, 152.0 ppm respectively). Thus, the assumption of a 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. Similarly, $\delta_{ap,Tol}$ and $\delta_{eq,Tol}$ were estimated to be 155.5 and 135.5 ppm, 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 (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 depend mainly on the number of Ar (or Tol) groups and not their position (apical or equatorial). This indicates that the apicophilicity of Ar and Tol groups should be almost the same at 60 °C. Consequently, that the rate of pseudorotation is fast at 60 °C, making the difference between Ar or Tol groups negligible, whereas pseudorotation is slow at −80 °C and the positions of the Ar or Tol groups are in equilibrium according to apicophilicity.

Disproportionation reaction: To certify that no intermolecular reaction takes place during the LCR, a mixture of **1** and **6** was heated in [D$_6$]benzene at 60 °C. Contrary to our expectations, in the ^{19}F NMR spectra five peaks appeared that were identified as those for **2**–**6** by comparison with the authentic samples. 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 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 through the mechanism shown in Scheme 10. By using "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 concomitant mutual exchange of aryl groups by 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 consid-



Scheme 10. Halogenoantimony-assisted disproportionation.



Scheme 11. Proposed mechanism for the LER.

ered to be a characteristic reaction for the hypervalent bond.

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).

To determine the relative stability of pentaarylantimony compounds in solution, a variety of mixtures of Tol_5Sb (**1**) and Ar_5Sb (**6**) in differing molar ratios in [D$_6$]benzene were heated at 60 °C to effect the ligand-exchange equilibrium. In these solutions, 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 spectra. The statistical (theoretical) molar ratios in equilibrium were calculated by the following Equations (1)–(3), derived by the use of combinatorial theory (a: initial mole of Ar_5Sb, t: initial mole of Tol_5Sb, N_A: Avogadro's number).

$$Tol_5Sb : ArTol_4Sb : Ar_2Tol_3Sb : Ar_3Tol_2Sb : Ar_4TolSb : Ar_5Sb \tag{1}$$

$$= {}_{5tN_A}C_5 : {}_{5tN_A}C_4 \times {}_{5aN_A}C_1 : {}_{5tN_A}C_3 \times {}_{5aN_A}C_2 : {}_{5tN_A}C_2 \times {}_{5aN_A}C_3 : {}_{5tN_A}C_1 \times {}_{5aN_A}C_4 : {}_{5aN_A}C_5 \tag{2}$$

$$\approx t^5 : 5t^4a : 10t^3a^2 : 10t^2a^3 : 5ta^4 : a^5 \tag{3}$$

The experimental ratio of Tol_5Sb, which cannot be observed in ^{19}F NMR spectroscopy, 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 $t/a=2.74$, in which t = the initial amount of the Tol_5Sb (**1**), 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 **6** was very small, thus, the stability constants for **6** potentially include a large experimental error.

Table 4. Equilibrium ratio resulting 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**) $\approx t^5S_0:5t^4aS_1:10t^3a^2S_2:10t^2a^3S_3:5ta^4S_4:a^5S_5$.

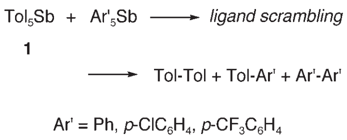
	1	2	3	4	5	6
statistical ratio	0.753	1.373	1.00	0.367	0.0667	0.00467
observed ratio	0.590	0.835	1.00	0.193	0.0275	0.00413
S_i[a]	0.780	0.608	1.00	0.526	0.410	0.846

[a] Relative stability constant ($i=0$–5).

As the observed ratio of **1** relies on the accuracy of **2**–**6**, it follows that the stability constant for **1** may also include a 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. 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** shown in Table 5 should have the same value, a priori. The large ambiguity in the values given for **1** stems from the fact that **1** cannot be directly observed in ^{19}F NMR spectroscopy and that the amount of **1** was estimated from the quantity of other compounds, as described above. The discrepancy in the value for **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 that **3** has the highest stability can be explained by considering the electron-donating properties of the three equatorial p-methylphenyl groups and the electron-withdrawing properties of the two apical p-trifluoromethylphenyl groups. The stability order shows that 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.

Uncatalyzed ligand-coupling reactions (LCRs) from mixed pentaarylantimony compounds in solution

LCR from the equilibrated mixture of mixed pentaarylantimony compounds: We found that the LER took place at much lower temperatures (ca. 60 °C) than the LCR (ca. 160 °C). Therefore, we examined the LCR of an 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, was almost identical to the statistical ratio (Figure S1, see the Supporting Information). This result was consistent with those reported for similar LCRs from a mixture of Ph_4Te and



Scheme 12. LCR of equilibrated mixtures.

Tol_4Te.[14] However, upon use of a mixture of Tol_5Sb (**1**) and (p-$ClC_6H_4)_5Sb$, 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). In the case of Tol_5Sb (**1**) and (p-$CF_3C_6H_4)_5Sb$ (**6**), the preference for the formation of Tol−Ar by the sacrifice of the Tol−Tol became more apparent (Figure 7).

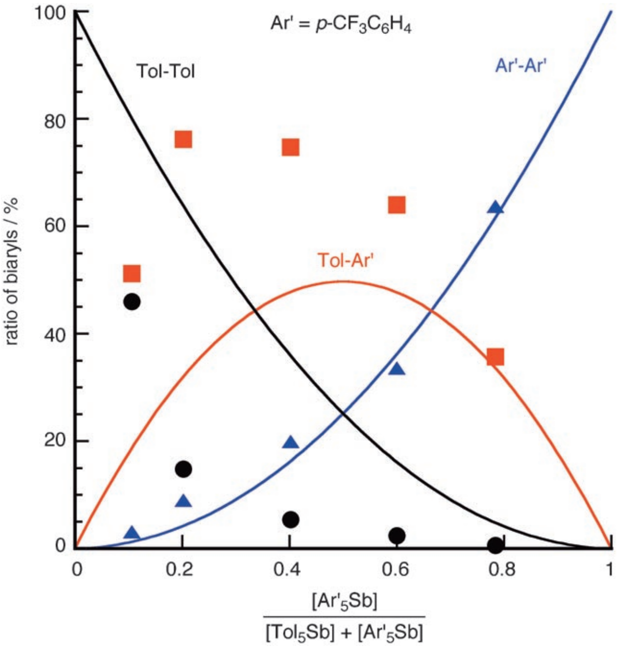


Figure 7. Distribution of biaryls generated from the LCR using a mixture of **1** and **6**. ●, ■, and ▲: experimental ratio of Tol-Tol, Tol-Ar′, and Ar′-Ar′, respectively. Solid lines: calculated statistical ratios.

As ^{19}F NMR spectroscopy is easy to monitor, we chose (p-$CF_3C_6H_4)_5Sb$ (**6**) to investigate the LCR with the prospect of calculating the selectivities of the LCR from a mixture of Tol_5Sb (**1**) and Ar_5Sb (**6**) in differing molar ratios in [D_6]benzene. As mentioned above, ligand-exchange (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: 1) the LE equilibration was fast and equilibration was maintained throughout the LCR, and 2) the rate of the LCR was the same for all of the mixed pentaarylantimony compounds. Monitoring the LCR by using ^{19}F NMR spectroscopy revealed, however, that the rate of the LCR from compounds having more Ar groups (such as **5** and **6**) was much slower than those from Tol_5Sb (**1**) or $ArTol_4Sb$ (**2**). Therefore, the fundamental assumptions of 2) and certainly 1) 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:[3,5-$(CF_3)_2C_6H_3]_4B$): To determine the selectivity of the LCR for each pentaarylantimony complex, it was necessary to find experimental conditions that 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 transmetalation of the phenyl group to the copper atom could not be avoided. Therefore, we searched for catalysts capable of acceleration without the possibility of transmetalation and found anhydrous Li^+TFPB^-, whereas LiBr and LiCl were not effective at all. Anhydrous LiTFPB, previously synthesized by Sonoda et al., 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 using the lithium cation as a catalyst, the transmetalation was expected not to take place because the formation of $Ar_4Sb{\cdot}ArLi{\cdot}TFPB^-$ 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 LCRs from **1** and **6** were dramatically accelerated by $Cu(acac)_2$, reactions being completed within 5 min at 165 °C. However, for **2**–**5**, the LE side reaction occurred more (ca. 20 %) for $Cu(acac)_2$ than for LiTFPB. This result may have come from the contribution of transmetalation of the aryl group to the copper, and moreover, there is the possibility of biaryl formation from arylcopper species generated by transmetalation. Therefore, we chose LiTFPB as the catalyst to avoid complexity.

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

The LCR catalyzed by LiTFPB was applied to mixed pentaarylantimony compounds (**2**–**5**). Experimental ratios of biaryls and triarylantimony compounds were determined by GC and relative integral intensities in the ^{19}F NMR spectra. Bitolyl (Tol−Tol) was not formed at all from Ar_2Tol_3Sb (**3**), Ar_3Tol_2Sb (**4**), or Ar_4TolSb (**5**), as shown in Table 7. Although bitolyl was obtained from the LCR of $ArTol_4Sb$ (**2**), we believe that bitolyl should be formed from Tol_5Sb (**1**) because the LE rate of **2** was found to be exceptionally fast. The LER product percentages are shown in the last column of Table 7 and are 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 formed, which should be a product of LC after LE of Ar_3Tol_2Sb (**4**). The percentage of LER was estimated to be at least 12 % because equal quantities (6 %) of $ArTol_4Sb$ (**2**) and Ar_3Tol_2Sb (**4**) should be formed. As $ArTol_2Sb$ should also be formed from Ar_2Tol_3Sb

Table 7. LCR catalyzed by LiTFPB (TFPB:[3,5-$(CF_3)_2C_6H_3]_4B$).[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 conditions: C_6D_6 at 165 °C, sample concentration 0.011–0.034 M. [b] Reaction time = 3.5 h. [c] Reaction time = 10 min.

(**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**.

The catalytic effect of the Li^+ cation can be rationalized by assuming coordination of the cations with 1) the fluorine atom in the CF_3 group, 2) the benzene ring of the tolyl and/or the aryl group, or 3) the electron-rich apical Sb–C bond. As high catalytic activity was observed for Tol_5Sb (**1**) relative to Ar_5Sb (**6**) (see Table 6), the coordination of the Li^+ cation to the benzene ring of the tolyl group, or the electron-rich apical Sb–C bond, should be the 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 (see below), 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 to a certain extent with the catalytic LCR from each of $Ar_nTol_{5-n}Sb$. Therefore, to obtain conclusive results for the selectivity in the LCR from only one specified species, we chose to perform LCR in its vapor phase, in which the collision of molecules (that cause 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 introduced to the oven (300 °C) for the LCR. Details of 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).

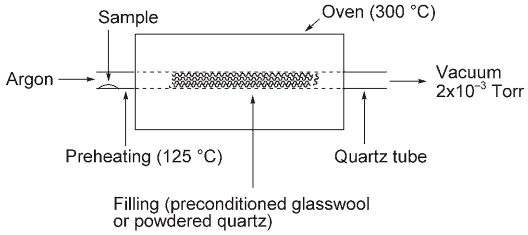


Figure 8. Flash vacuum thermolysis (FVT) apparatus.

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

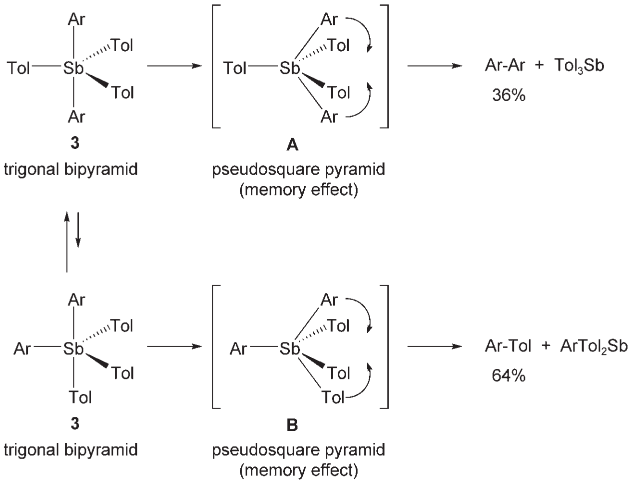
Oven temp. [K]	Ar–Ar	Ar–Tol	Tol–Tol
300	58 ± 1.9	42 ± 1.9	0
250	59	41	0
200	61	39	0
statistical ratio	30	60	10

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

The results of the FVT experiments 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 by the LCRs, 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 fillings (crushed quartz glass pretreated with "coating", see Experimental Section). Protonolysis is 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 due to very fast LERs ($2\,ArTol_4Sb \rightarrow Tol_5Sb + Ar_2Tol_3Sb$). 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.

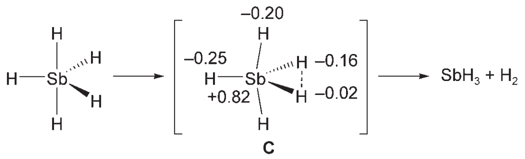
The fact that Tol–Tol could not be detected at all from Ar_4TolSb (**5**), Ar_3Tol_2Sb (**4**), or Ar_2Tol_3Sb (**3**) rules out the possibility of a LCR taking place through equatorial–equatorial coupling, because **3** and **4** would be expected to produce Tol–Tol if the equatorial–equatorial coupling was in operation. If apical–equatorial coupling was in operation, **3** and **4** would be expected to give rise to small but definite amounts of Tol–Tol from a less stable stereoisomer, which should be present to a certain extent by BPR. There is an apparent trend for the more-electronegative $p\text{-}CF_3C_6H_4$ group to preferentially 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 the LCR to give Ar−Tol is faster than that of Ar−Ar. This is consistent with the results 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 pathway. That is, once the apical substituents start a bending motion for the LCR, the pairing is maintained through the transition state onto the final products with the conservation of the momentum, that is, 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. The mechanism of the apical–apical LCR is illustrated in Scheme 13, using Ar_2Tol_3Sb (**3**) as an example.



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

In addition, there is a general preference for the more electronegative substituents, which probably occupy the apical sites, to participate in the LCRs. 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, accompanied by a decrease in PhC≡C−C≡CPh.

Recent advanced ab initio calculations predicted that the LCR of SbH_5 proceeds in a manner of equatorial–equatorial coupling through transition state **C**, as shown in Scheme 14.[11] The departing dihydrogens in the equatorial positions were shown to have less electron density than that of other hydrogens in transition state **C**. 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 groups by using hydrogens in the place of carbons in the calculation.



Scheme 14. Reaction mode of LCR predicted by theoretical calculations.[11]

In regard to 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 an intermediate, and on to a product that is closest through a straight-line pathway to conserve momentum.[37] Further theoretical studies are necessary to make clear the reasons for the present contradiction.

Conclusion

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

The ligand-exchange reaction (LER), instead of the ligand-coupling reaction (LCR), was found to take place upon heating a mixture of pentaaryantimony complexes at 60 °C in solution. 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 unique to hypervalent compounds, being consistent with the nature of hypervalent bonding.

The ligand-coupling reaction (LCR) took 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 flash vacuum thermolysis (FVT) experiments. The results were essentially the same as those obtained with the catalytic LCR in solution. We concluded that apical–apical coupling is the sole process of LCR for pentaarylantimony compounds.

Experimental Section

General: ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (100 MHz) spectra were recorded by using a JEOL EX-400 spectrometer. ^{1}H NMR (90 MHz) and ^{19}F NMR (85 MHz) spectra were also routinely recorded by using a Hitachi R-90H spectrometer. Chemical shifts are reported (δ scale) from an internal tetramethylsilane reference for ^{1}H and ^{13}C or from an external fluorotrichloromethane reference 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 2–5: The apparatus for FVT is shown in Figure 8. A mixed pentaarylantimony compound (10–15 mg) was placed at the head of a quartz tube in which "fillings" were packed in the center. "Fillings" were crushed quartz glass pretreated with "coating" to avoid protonolysis and any catalyzed reaction on the surface of the fillings. "Coating" means that the fillings were boiled in a benzene solution of a mixture of Ar_5Sb, Tol_5Sb, Ar_3Sb, Tol_3Sb, Tol_2, etc., overnight and the "fillings" were washed out thoroughly with acetone and deionized water and dried. The residual compounds were not detected at all by heating the quartz tube with the "fillings" up to 300 °C for several hours at high vacuum (10^{-5} Torr). The FVT tube was evacuated first to $1–2\times10^{-5}$ Torr with an oil diffusion pump and the pressure was kept at $1–2\times10^{-3}$ 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 that did not vaporize was analyzed by NMR spectroscopy 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 is presented with probable errors (see Table 9). The data for $ArTol_4Sb$ is an average of two runs.

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