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# METAL—HALOGEN BONDING STUDIES WITH GROUP IVA TRIALKYLMETAL HALIDES

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## Summary

Halogen redistribution reactions have been found to take place between benzyl bromide or benzyl iodide and the Group IVA silicon, germanium, tin, and lead containing trialkylmetal chlorides. However, for the reactions of the Si, Ge and Sn compounds, a quaternary ammonium halide catalyst was necessary to enable the equilibria to be established at reasonably rapid rates. The equilibrium constants at 50°C have been measured for each of these halogen redistributions. They have been found to increase gradually on going down in Group IVA from silicon to lead, being considerably less than unity in the case of silicon and somewhat greater than unity in the case of lead for both the $R_3MCl$ + BzBr and $R_3MCl$ + BzI reactions. The $\Delta G^0$ values for these equilibria have been calculated, and it is suggested that their differences may be explained in terms of the relative importance of $p_\pi$—$d_\pi$ contributions to the halogen—metal bonding in the various Group IVA trialkylmetal halide systems.

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## Introduction

We recently reported [1,2] studies of a new reaction discovered in our laboratory involving halogen redistributions [3] between carbon of alkyl halides and tin of tri-n-butyltin halides. For example, the reaction of benzyl bromide with tri-n-butyltin chloride, neat, in a 1/1 mol ratio at 50°C in the presence of a quaternary ammonium bromide catalyst proceeded to give an equilibrium mixture containing about 64% of benzyl chloride and tri-*n*-butyltin bromide and 36% of benzyl bromide and tri-n-butyltin chloride (eq. 1). Evidence was presented to show

$$Bu_3SnCl + C_6H_5CH_2Br \xrightleftharpoons{K_{eq} = \text{ca. } 3} Bu_3SnBr + C_6H_5CH_2Cl \qquad (1)$$

that the mechanism of this reaction involves initial coordination of bromide ion with the tri-n-butyltin chloride to form a nucleophilic anionic complex containing pentavalent tin. This is then reactive for backside displacements at carbon of sterically unhindered alkyl halides.

The fact that these halogen redistributions between tin and carbon proceed to measurable equilibrium positions pointed to an interesting possible synthetic and theoretical study. Thus, similar halogen redistribution reactions might also be expected to occur for the trialkylmetal halides of Si, Ge and Pb. If so, using a common alkyl halide system as a reference standard for the reactions of all of the Group IVA trialkylmetal halides, from the equilibrium positions of the various reactions it was felt that thermodynamic information of value in connection with the interesting and important question of possible similarities or differences in the nature of the metal—halogen bonding with the different metals and halogens might be able to be uncovered. Our investigations into this possibility are described below.

## Results

For our studies of the halogen redistribution reactions between carbon of alkyl halides and metal of the Group IVA trialkylmetal halides of Si, Ge, Sn and Pb, we chose in all cases to examine either directly or indirectly the reactions of the readily available trialkylmetal chlorides with benzyl bromide and with benzyl iodide (eq. 2). The choice of the benzyl halides as the reference standard

$$R_3MX + C_6H_5CH_2X' \rightleftharpoons R_3MX' + C_6H_5CH_2X \qquad (2)$$

(M = Si, Ge, Sn, Pb; X = Cl, X' = Br, I)

was primarily because their reactions could be followed conveniently on small scale using NMR techniques not requiring any workup.

On initiating our studies with the reactions of trimethylsilicon halides and benzyl halides, we were gratified to find that the halogen redistributions between silicon and carbon did indeed take place. As was the case in our earlier work on the tri-n-butyltin halides [2], quaternary ammonium halides here also strongly catalyzed the reactions. Thus, at 50°C in the presence of about 5 mol percent of a tetra-n-butylammonium halide catalyst, the reactions were essentially completed within several hundred minutes. In the absence of the catalyst no reaction took place even after extended periods under otherwise similar reaction conditions. Also, irradiation with ultraviolet light, while taking care to maintain the reaction temperature at 50°C, produced no significant acceleration in the reaction rate [4].

Table 1 summarizes the results of our investigations with the trimethylsilicon halides. Using 1/1 mol ratios of reactants, equilibrium positions were reached which were either too large or too small for highly accurate equilibrium constants to be calculated. Thus, for several of the halide combinations larger mol ratios of the reactants were necessary. However, this fact points to the interesting possibility that trimethylsilicon iodide, which is now commercially available, might be used on a synthetic scale for converting alkyl chlorides or bromides to iodides of interest. This is currently under investigation.

For the reactions of trialkylgermanium chlorides with benzyl bromide or iodide, quaternary ammonium halides were again found to strongly catalyze the reactions. After 150 h at 50°C in the absence of the catalyst, a neat 1/1 mol ratio mixture of triethylgermanium chloride and benzyl bromide showed no

TABLE 1

THE REACTIONS OF TRIMETHYLSILICON HALIDES WITH BENZYL HALIDES IN THE PRESENCE OF A 5 mol % TETRA-n-BUTYL AMMONIUM HALIDE CATALYST AT 50°C IN THE ABSENCE OF A SOLVENT

| $(CH_3)_3SiX$, X = | $C_6H_5CH_2X'$, X' = | Mol Ratio $(CH_3)_3SiX/C_6H_5CH_2X'$ | $\%C_6H_5CH_2X$ at equilibrium ±2% | $K_{eq}$ |
|---|---|---|---|---|
| Cl | Br | 1/1 | 7 | 0.0057 ± 0.0029 |
| Cl | Br | 5/1 | 16 | 0.0063 ± 0.0019 |
| Cl | Br | 10/1 | 22 [a] | 0.0063 ± 0.0015 |
| Br | Cl | 1/1 | 93 [a] | 0.0057 ± 0.0029 [b] |
| Cl | I | 1/1 | ca. 0 | <0.0004 |
| I | Cl | 1/1 | ca. 100 | <0.0004 [b] |
| Br | I | 1/1 | 8 [a] | 0.0076 ± 0.0047 |
| Br | I | 5.3/1 | 16 | 0.0060 ± 0.0017 |
| Br | I | 9.9/1 | 21 | 0.0058 ± 0.0014 |
| I | Br | 1/1 | 92 | 0.0076 ± 0.0047 [b] |

[a] Values given are averages for reactions run at least in duplicate. [b] Calculated for the reactions run in the reverse direction than as written.

detectable reaction. However, in the presence of 5 mol percent of *N*-benzylpyridinium bromide, the reaction went to completion in less than 6.5 h.

The results from the present investigation for the reactions with the trialkylgermanium chlorides are summarized in Table 2. It is noteworthy that both the triethyl and tri-n-butylgermanium chlorides proceed to similar equilibrium positions. This indicates that primarily electronic and not steric or halogen bridging effects must be manifested in the results and thus they are comparable with the trimethylsilicon halide results. A comparison of the trimethylsilicon halide and triethyl or tri-n-butylgermanium halide data clearly shows the much greater preference of chlorine relative to bromine or iodine for bonding with silicon rather than with germanium.

Table 3 summarizes the results of our studies with trialkyl or triaryl substituted tin halides. Here, because of our special interests in the properties and chemistry or organotin compounds, our investigations have been carried out in somewhat greater detail than for the other metals. Also, with the trialkyltin halides, it was necessary to consider the possibility of differential halogen bridging effects [5] on the equilibrium positions.

With the trimethyltin halides, where the chloride is a solid and halogen bridging must obviously be important, it is seen that the equilibrium positions indeed were dependent on reactant concentrations in solution. This is especially the the case with the trimethyltin chloride/benzyl iodide reaction, and would be expected since halogen bridging effects in the tin chloride should not be balanced by similar effects in the corresponding tin iodide. Just why, however, the acetonitrile solvent appears at first glance to be less effective than the n-heptane at preventing halogen bridging effects is unknown. Perhaps this is a result of acetonitrile itself being involved in coordination with the tin halides in a manner which, as with the halogen bridging, appears to stabilize the tin chloride relative to the tin bromide or tin iodide.

In considering the triethyltin and tri-n-butyltin halide results, it is seen that

TABLE 2

THE REACTIONS OF TRIETHYL AND TRI-n-BUTYLGERMANIUM CHLORIDES WITH BENZYL HALIDES IN THE PRESENCE OF A 5 mol % *N*-BENZYL PYRIDINIUM HALIDE CATALYST AT 50°C IN THE ABSENCE OF A SOLVENT

| $R_3GeCl$, R = | $C_6H_5CH_2X'$, X' = | Mol Ratio $R_3GeCl/C_6H_5CH_2X'$ | %$C_6H_5CH_2Cl$ at equilibrium ±2% | $K_{eq}$ |
|---|---|---|---|---|
| Ethyl | Br | 1/1 | 44 [a] | 0.62 ± 0.11 |
| Ethyl | I | 1/1 | 12 [a] | 0.019 ± 0.008 |
| Ethyl | I | 20/1 | 43 [a] | 0.017 ± 0.002 |
| n-Butyl | Br | 0.6/1 | 36 [a] | 0.84 ± 0.22 |
| n-Butyl | Br | 1/1 | 43 [a] | 0.57 ± 0.10 |
| n-Butyl | I | 1/1 | 10 | 0.012 ± 0.007 |
| n-Butyl | I | 20/1 | 48 [a] | 0.023 ± 0.003 |

[a] Values given are averages for reactions run at least in duplicate.

even when "neat" they are similar to those at high dilution for the trimethyltin halides. This is as expected since, with the bulkier ethyl and n-butyl groups around tin, even the chlorides are liquids and thus halogen bridging must be minimal. Also, because of the long bond lengths, steric effects on the tin—halogen bonding would be expected to be negligible [6]. Thus, since methyl, ethyl and n-butyl groups exhibit similar electronic substituent effects, in the absence of

TABLE 3

THE REACTIONS OF SOME TRISUBSTITUTED TIN HALIDES WITH BENZYL HALIDES IN A 1/1 MOL RATIO AT 50°C IN THE PRESENCE OF A 5 mol % *N*-BENZYL PYRIDINIUM HALIDE CATALYST

| $R_3SnX$ | $C_6H_5CH_2X'$, X' = | Solvent | $[R_3SnX]$, (*M*/l) | %$C_6H_5CH_2X$ at equilibrium ±2% | $K_{eq}$ |
|---|---|---|---|---|---|
| $Me_3SnCl$ | Br | Neat | — | 60 [a] | 2.2 ± 0.5 |
| $Me_3SnCl$ | Br | n-Heptane | 1.0 | 61 | 2.4 ± 0.5 |
| $Me_3SnCl$ | Br | n-Heptane | 0.51 | 62 | 2.7 ± 0.5 |
| $Me_3SnCl$ | Br | n-Heptane | 0.26 | 62 | 2.7 ± 0.5 |
| $Me_3SnCl$ | Br | $CH_3C{\equiv}N$ | 1.0 | 59 | 2.1 ± 0.4 |
| $Me_3SnCl$ | Br | $CH_3C{\equiv}N$ | 0.50 | 60 | 2.2 ± 0.5 |
| $Me_3SnCl$ | I | Neat | — | 21 [a] | 0.070 ± 0.020 |
| $Me_3SnCl$ | I | n-Heptane | 1.0 | 27 | 0.14 ± 0.03 |
| $Me_3SnCl$ | I | n-Heptane | 0.55 | 28 | 0.15 ± 0.03 |
| $Me_3SnCl$ | I | n-Heptane | 0.26 | 29 | 0.17 ± 0.03 |
| $Me_3SnCl$ | I | $CH_3C{\equiv}N$ | 1.0 | 21 | 0.070 ± 0.020 |
| $Me_3SnCl$ | I | $CH_3C{\equiv}N$ | 0.51 | 21 | 0.070 ± 0.020 |
| $Et_3SnCl$ | Br | Neat | — | 63 [a,b] | 2.9 ± 0.5 |
| $Et_3SnCl$ | I |  | — |  | (0.32 ± 0.15) [c] |
| $Et_3SnBr$ | I | Neat | — | 25 [a] | 0.11 ± 0.03 |
| $n\text{-}Bu_3SnCl$ | Br | Neat | — | 63 [a] | 2.9 ± 0.5 |
| $n\text{-}Bu_3SnCl$ | I | Neat | — | 32 [a] | 0.22 ± 0.05 |
| $n\text{-}Bu_3SnBr$ | I | Neat | — | 26 [a] | 0.12 ± 0.03 |
| $(C_6H_5)_3SnCl$ | Br | $CH_3C{\equiv}N$ [d] | 0.67 | 61 [a] | 2.4 ± 0.5 |
| $(C_6H_5)_3SnCl$ | I | $CH_3C{\equiv}N$ [d] | 0.55 | 35 [a] | 0.29 ± 0.05 |

[a] Values given are averages for reactions run at least in duplicate. [b] Calculated from data for a reaction run in the reverse direction than is indicated. [c] Calculated from the other two values using the equation $K_{eq}(SnCl + CI) = K_{eq}(SnBr + CI) \times K_{eq}(SnCl + CBr)$. [d] Done at 100°C to achieve solubility.

TABLE 4

THE REACTIONS OF TRIETHYLLEAD CHLORIDE WITH BENZYL HALIDES IN 1/1 mol RATIOS AT 50°C IN THE PRESENCE OF A 5 mol % *N*-BENZYL PYRIDINIUM HALIDE CATALYST

| $R_3PbX$ | $C_6H_5CH_2X'$, $X'$ = | Solvent [a] | $[R_3PbX]$, *M*/l | %$C_6H_5CH_2Cl$ at equilibrium ±2% | $K_{eq}$ |
|---|---|---|---|---|---|
| $Et_3PbCl$ | Br | Toluene | 4.0 | 80 | 16 ± 5 |
| $Et_3PbCl$ | Br | n-Heptane | 1.0 | 79 | 14 ± 4 |
| $Et_3PbCl$ | Br | n-Heptane | 0.52 | 80 | 16 ± 5 |
| $Et_3PbCl$ | Br | n-Heptane | 0.26 | 83 | 24 ± 8 |
| $Et_3PbCl$ | Br | $CH_3C{\equiv}N$ | 1.0 | 82 | 21 ± 7 |
| $Et_3PbCl$ | Br | $CH_3C{\equiv}N$ | 0.50 | 83 | 24 ± 8 |
| $Et_3PbCl$ | I | Toluene | 6.0 | 68 | 4.5 ± 1.0 |
| $Et_3PbCl$ | I | n-Heptane | 1.0 | 71 | 6.0 ± 1.4 |
| $Et_3PbCl$ | I | n-Heptane | 0.52 | 76 | 10 ± 3 |
| $Et_3PbCl$ | I | n-Heptane | 0.26 | 82 | 21 ± 7 |
| $Et_3PbCl$ | I | $CH_3C{\equiv}N$ | 1.1 | 74 | 8.1 ± 1.9 |
| $Et_3PbCl$ | I | $CH_3C{\equiv}N$ | 0.55 | 76 | 10 ± 3 |

[a] No "neat" reactions were run because of solubility problems.

other factors one would expect them to behave similarly as observed.

Finally for the tin system we also looked briefly at the triphenyltin halides to determine if any electronic substituent effects of the phenyl groups could be detected. Because of solubility problems, it was necessary to run the reactions in acetonitrile solvent and at 100°C. However, the equilibrium positions attained were similar to those for the corresponding triethyl- and tri-n-butyl-tin halide cases indicating the absence of any special electronic effects of the phenyl groups.

The redistribution reactions of triethyllead chloride with the benzyl halides proceeded well even in the absence of a quaternary ammonium halide catalyst. However, for consistency, all of the reactions were still run in the presence of a small amount of an *N*-benzylpyridinium halide. Here, as with the trimethyltin halides, the problem of halogen bridging effects needed to be considered. Thus, the results in Table 4 indicate that the positions of equilibrium attained in solution for the reaction of triethyllead chloride with benzyl bromide and benzyl iodide are clearly dependent on the reactant concentrations. Even further dilutions than those shown would have been desirable to ascertain the equilibrium positions in the absence of any halogen bridging effects. However, this was not possible owing to analytical difficulties at the lower concentrations. Nevertheless, from the results obtained, it can be established that the equilibrium constants for the reactions as written are all considerably higher for the triethyllead halides than for the corresponding Si, Ge and Sn cases. This appears to be part of a definite trend on going down the Group IVA series.

## Discussion

To facilitate comparisons of the Group IVA metal—halogen bonding effects uncovered in the present study, the summary given in Table 5 has been prepared. Here, for each of the trialkylmetal halide plus benzyl halide reaction types, selected $K_{eq}$ values from Table 1—4 are listed which it is felt best represent the behavior expected for the reactions in the absence of any steric or halogen bridging effects. The $\Delta G^0$ values given were calculated using these representative $K_{eq}$ values. For those reactions where experimentally determined $K_{eq}$ values were not available, the missing $\Delta G^0$ values were calculated as shown in eq. 3 from the other two $\Delta G^0$ values. The trends in the $\Delta G^0$ values are depicted graphically in Fig. 1.

$$\Delta G^0(\mathrm{MBr + CI}) = \Delta G^0(\mathrm{MCl + Cl}) - \Delta G^0(\mathrm{MCl + CBr}) \tag{3}$$

Before commenting on the magnitudes and trends for the $\Delta G^0$ values of the various trialkylmetal halide plus benzyl halide reactions, it is necessary to briefly consider their theoretical meaning. If the $\Delta S^0$ values for all of the reactions are equal to zero, as might be expected for equilibria of the type under consideration where the species on both sides of the equilibria do not differ in molecularity and vary only slightly in structure, $\Delta G^0 = \Delta H^0$. This expectation of zero $\Delta S^0$ values for all of the reactions is supported by the observation [7] that for the reactions of tri-n-butyltin chloride both with benzyl bromide and with benzyl iodide the $\Delta G^0$ values were found within experimental error to be invarient with temperature over the range of 50 to 150°C. Finally, the $\Delta G^0 = \Delta H^0$ values can be related to the C—X and M—X bond dissociation energies ($DH^0$ values of the benzyl and trialkylmetal halides) by eq. 4 given below. Thus, the

$$\Delta H^0 = [DH^0(\mathrm{R_3M{-}X}) - DH^0(\mathrm{R_3M{-}X'})] - [DH^0(\mathrm{C_6H_5CH_2{-}X}) \\ - DH^0(\mathrm{C_6H_5CH_2{-}X'})] \tag{4}$$

$\Delta G^0 = \Delta H^0$ values for the reactions represent the difference between a given MX—MX′ bond dissociation energy difference for the trialkylmetal halides and the corresponding CX—CX′ bond dissociation energy difference for the benzyl halides.

TABLE 5

A SUMMARY OF THE $K_{eq}$ AND $\Delta G^0$ VALUES FOR THE REACTION OF GROUP IVA TRIALKYLMETAL HALIDES WITH BENZYL HALIDES AT 50°C

| $R_3MX$ | $C_6H_5CH_2X'$, $X'$ = | $K_{eq}$ [a] at 323 K | $\Delta G^0$(kcal mol$^{-1}$) [b] at 323 K |
|---|---|---|---|
| $R_3SiCl$ | Br | 0.0063 ± 0.0015 | +3.2 ± 0.1 |
| $R_3SiBr$ | I | 0.0058 ± 0.0014 | +3.3 ± 0.1 |
| $R_3SiCl$ | I | | (+6.5) |
| $R_3GeCl$ | Br | 0.60 ± 0.10 | +0.3 ± 0.11 |
| $R_3GeBr$ | I | | (+2.2) |
| $R_3GeCl$ | I | 0.020 ± 0.003 | +2.5 ± 0.1 |
| $R_3SnCl$ | Br | 2.9 ± 0.5 | −0.7 ± 0.4 |
| $R_3SnBr$ | I | 0.11 ± 0.03 | +1.4 ± 0.1 |
| $R_3SnCl$ | I | 0.25 ± 0.05 | +0.9 ± 0.1 |
| $R_3PbCl$ | Br | >24 ± 8 | <−2.0 ± 0.2 |
| $R_3PbBr$ | I | | (+0.1) |
| $R_3PbCl$ | I | >21 ± 7 | <−1.9 ± 0.2 |

[a] Values selected from Tables 1—4 best representing the equilibrium positions in the absence of other than electronic effects. [b] Values in parentheses were calculated from the other two using the relationship: $\Delta G^0$(MBr + CI) = $\Delta G^0$(MCl + CI) — $\Delta G^0$(MCl + CBr).

That the above type of treatment and the assumptions behind it are valid is supported by the following results. Using the calorimetrically derived tin—halogen bond dissociation energies of Baldwin and coworkers [8] for the trimethyltin halides, $DH^0(\text{Me}_3\text{Sn—Cl}) - DH^0(\text{Me}_3\text{Sn—Br})$ and $DH^0(\text{Me}_3\text{Sn—Cl}) - DH^0(\text{Me}_3\text{Sn—I})$ can be calculated as 14 and 30 kcal $\text{mol}^{-1}$, respectively. These values are almost identical to those of 14.0 and 30.2 kcal $\text{mol}^{-1}$ which can be calculated using the $\Delta G^0 = \Delta H^0$ values we have measured for the trialkyltin halide reactions (eq. 4) and the carbon—halogen bond dissociation energies of 69.4, 54.7 and 40 kcal $\text{mol}^{-1}$, respectively for benzyl chloride, bromide, and iodide given in the tabulation of Egger and Cocks [9].

An inspection of the $\Delta G^0$ values tabulated in Table 5 and illustrated in Fig. 1, reveals that for the trimethylsilicon halide system the SiCl—SiI and SiBr—SiI bond dissociation energy differences are considerably enhanced relative to the corresponding differences for the carbon or other Group IVA element systems. Also, the enhancement for the SiCl—SiI difference is much greater than that for the SiBr—SiI difference. However, on going down in Group IVA, there appears to be a crossover after germanium leading finally to the PbBr—PbI bond dissociation energy difference of lead being the same as that for carbon but to slight depression of its PbCl—PhI bond dissociation energy difference relative to that for carbon.

A possible interpretation of the observed trends can be given in terms of the relative importance of $p_\pi$—$d_\pi$ contributions [10] to halogen—metal bonding with the different halogens and metals in the various trialkylmetal halides. Thus, if this type of bonding is much more important with silicon than with carbon, and if the importance of such bonding for the halogens lies as one might predict from bonding orbital sizes in the order Cl > Br > I, one would expect both the SiCl—SiI and SiBr—SiI bond dissociation energy differences to be enhanced rela-

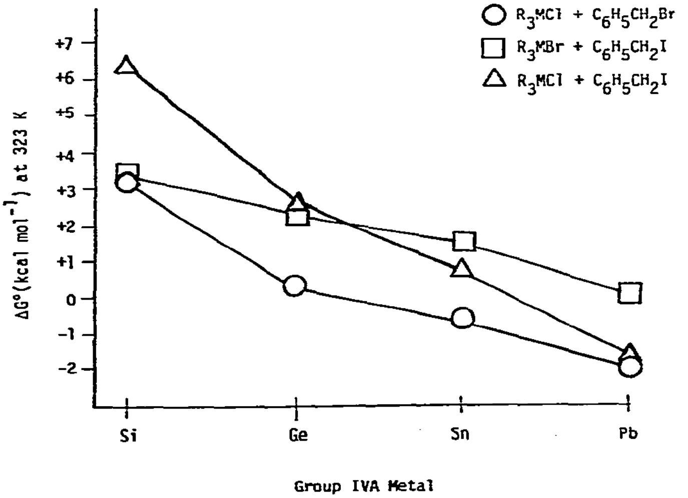

Fig. 1. Trends in $\Delta G^0$ at 323 K for the reactions of Group IVA trialkylmetal halides with benzyl halides.

tive to the corresponding values for carbon. However, the enhancement for the SiBr—SiI bond dissociation energy difference should be smaller than that for the SiCl—SiI difference as is observed.

It should be noted that similar conclusions regarding the possible importance of $p_\pi$—$d_\pi$ contributions to Si—Cl and Si—Br bonding have been reached by others. For example, Baldwin, Lappert, Pedley and Poland [8] reported a study showing the trends in mean metal—halogen bond dissociation energies for C, Si, Ge and Sn systems as determined from calorimetric measurements. Here they noted enhancements for $\bar{E}$(SiCl) and $\bar{E}$(SiBr) relative to the corresponding values for the other Group IVA elements. Also, Moedritzer and Van Wazer [11] have observed in their investigations of the exchange of halogens between dimethylsilicon and dimethylgermanium moieties the preference for chlorine relative to bromine and bromine relative to iodine to reside on silicon rather than on germanium. In fact, from examination of their data, it can be seen that the preference appears to be energetically even greater than with our trimethylsilicon halides by about 3 kcal $mol^{-1}$ in each category. However, the reason for the larger effects with the dimethylsilicon halides is not obvious.

Considering the data for the other trialkylmetal halide systems given in Table 5 and depicted in Fig. 1, it is not surprising that metal—halogen bond dissociation energy difference enhancements due to the importance of $p_\pi$—$d_\pi$ halogen—metal bonding interactions should decrease on going down in Group IVA from silicon to lead. However, observation of the apparent crossover in the MCl—MI and MBr—MI bond dissociation energy difference enhancements between germanium and tin, and continuing with lead, was unexpected and to the best of our knowledge has not been previously reported. Although the energy differences are small, we believe they are meaningful in light on the sensitivity of the equilibrium method we have employed. A possible interpretation might be that with Ge, Sn and Pb the $p_\pi$—$d_\pi$ bonding contributions are progressively becoming relatively more important with the M—Br and possibly M—I bonds, but relatively less important with the M—Cl bonds. This is what might be expected in terms of the relative energy levels and sizes of the bonding orbitals involved in these systems.

## Experimental

### *Materials*

Most of the trialkylmetal halides and benzyl halides employed in the study were obtained commercially and if necessary redistilled or recrystallized before use. Benzyl iodide, however, was prepared by reaction of benzyl chloride with potassium iodide in acetone, b.p. 52—53°C/0.5 mmHg, $n_D^{22}$ 1.6342 (lit. [12] b.p. 98—102°C/14 mmHg, $n_D^{17.2}$ 1.6667). Trimethylsilicon bromide was prepared by dropwise addition of bromine to hexamethyldisilane; b.p. 81—82°C/750 mmHg, $n_D^{21}$ 1.4243 (lit. [13] b.p. 77.3°C/735 mmHg, $n_D^{25}$ 1.4211). Trimethylsilicon iodide was prepared by adding iodine to hexamethyldisilane and after 2 h at 60—65°C the $Me_3SiI$ was distilled from aluminum turnings; b.p. 105—107°C/750 mmHg, $n_D^{21}$ 1.4721 (lit. [14] b.p. 106.5°C/734 mmHg). Tri-n-butyltin bromide was prepared as described previously [1].

### *General equilibration procedure*

All reactions were run on millimole scale in sealed NMR tubes. The reaction mixtures were heated at 50 ± 1°C in a constant temperature bath and periodically removed for direct proton NMR examination without any prior work-up. The course of the reactions was followed by observing the changes in the benzylic protons of the benzyl halides using the aromatic proton absorption as an internal standard. The approximate chemical shift positions of the benzylic protons for the various benzyl halides were $C_6H_5\underline{CH}_2Cl$, $\delta$ 4.4(s); $C_6H_5C\underline{H}_2Br$, $\delta$ 4.3(s); and $C_6H_5C\underline{H}_2I$, $\delta$ 4.3 ppm(s). These varied slightly, however, in different reaction mixtures, although in all cases they could actually be resolved sufficiently for accurate analyses in two halide containing reaction mixtures. After about ten half lives for reaction when it was observed that stable equilibrium positions had clearly been established, the compositions of the benzyl halides in the equilibrium mixtures were carefully determined using the averages of at least five NMR integrations of the proton regions of interest. Whenever possible full scale integrals were employed for highest accuracy. In selected cases, isolation, chromatographic examination or spectrometric methods were employed to confirm the natures of the trialkylmetal halides present in the reaction mixtures. However, for equilibrium constant calculations the actual amounts of trialkylmetal halides and benzyl halides present were calculated assuming that $BzX_e + BzX'_e = BzX'_i$; $R_3MX_e + R_3MX'_e = R_3MX_i$; and $R_3MX'_e = BzX'_i - BzX'_e$, where "*i*" refers to initially weighed in quantities of reactants and "*e*" refers to the quantities of materials present in the reaction mixture after equilibrium has been established.

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