Journal of Organometallic Chemistry, 93 (1975) 139—171
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

EQUILIBRIA OF REDISTRIBUTION REACTIONS IN GROUP IVB ORGANOMETALLIC COMPOUNDS

K.P. BUTIN, V.N. SHISHKIN, I.P. BELETSKAYA and O.A. REUTOV
Physical Organic Laboratory, Chemical Department, Moscow State University, Moscow (U.S.S.R.)

(Received January 21st, 1975)

Summary

A method of predicting the position of equilibria of redistribution reactions of Group IVb organometallic compounds is presented. Equations are proposed in which the equilibrium constant is related to the difference in the pK_a values of the acids corresponding to the exchanging anions, and to the difference in affinity of the organometallic cations for the respective anions. For a large number of compounds the calculated positions of the equilibria are compared with experimental data available from the literature, good agreement being found in most cases. The proposed approach may be applied to equilibria in which organometallic compounds of other Groups in the Periodic Table participate.

I. Introduction

Reactions in which redistribution of organic (and inorganic) groups takes place are one of the most important methods for preparing various organometallic compounds. The general principle, which is commonly used in synthetic practice, involves the action of a salt of one metal on an organic compound of another, more electropositive, metal. However, such ligand exchange may also take place between metals that are similar or between two compounds of the same metal. Furthermore, examples exist which show that redistribution reactions may, depending on the nature of the exchanging organic group, R, and on the inorganic substituent, X or Y, groups, occur by means of R group transfer both from a more electropositive to a more electronegative and from a more electronegative to a relatively electropositive element. The following preparative reactions serve as illustrations [1-6]:

$$\left.\begin{array}{llll} \mathrm{RSnR'_3} & + \mathrm{HgX_2} \rightarrow & \mathrm{RHg} & + \mathrm{R'_3SnX} \\ \mathrm{RHgY} & + \mathrm{SnX_4} \rightarrow & \mathrm{RSnX_3} & + \mathrm{HgXY} \end{array}\right\}$$

$$\left.\begin{array}{llll} \mathrm{R_2Hg} & + \mathrm{BX_3} \rightarrow & \mathrm{RHgX} & + \mathrm{RBX_2} \\ \mathrm{R'_2BR} & + \mathrm{HgX_2} \rightarrow & \mathrm{R'_2BX} & + \mathrm{RHgX} \end{array}\right\}$$

There are a great number of papers nowadays concerning the different problems, e.g. preparative application, kinetics, stereochemistry and mechanism [7-15], of redistribution reactions. However, there is no sufficiently general concept which allows one to explain or predict a shift of equilibrium in each individual case.

In this paper we propose an approach to an explanation of redistribution equilibria in mixtures of Group IVb organometallic compounds. We consider relations between structure and position of the equilibrium, irrespective of the mechanism of the redistribution process. Although mechanisms of metal—R bond fission may be different for different redistribution processes (homolytic, or heterolytic in its variations: S_E2, S_E1, S_Ei, with ion-pair participation, etc.), the equilibrium of the redistribution reaction does not depend on the reaction mechanism.

Many quantitative data are available on equilibrium constants of ligand exchange in systems of Group IVb organometallic compounds; these data have been obtained by the use of various physical methods, but principally by NMR spectroscopy. All redistribution reactions may be divided "homo-redistribution" and "hetero-redistribution" processes:

$\text{m—R} + \text{m}'\text{—R} \rightleftharpoons \text{m—R} + \text{m}'\text{—R}$ (homo-redistribution)
$\text{m—R} + \text{m}'\text{—R}' \rightleftharpoons \text{m—R}' + \text{m}'\text{—R}$ (hetero-redistribution)

Homo-redistribution reactions result in products identical to the initial reactants, but the rates of such processes can be studied by NMR techniques or by using isotope labels. For homo-redistribution reactions equilibrium constants are always equal to unity. However, in spite of the obvious utility of these reactions for an elucidation of the effects of the ligands and the nature of the central metal atom on the rates of equilibrium attainment, homo-redistributions are not considered here, because this paper is devoted only to structural effects on redistribution equilibria.

A list of the different types of hetero-redistribution reactions is very long, if one takes into account that M and M′ may be different, that the eight groups bonded to M and M′ may all be different, and that the number of exchanging groups and stoichiometry of the reactions may be different too. The types of equilibria which have been experimentally studied up to the present are given below:

$$R^1R^2R^3MT + R^4R^5R^6M'Z \rightleftharpoons R^1R^2R^3MZ + R^4R^5R^6M'T \quad (1)$$
$$R^1R^2MT_2 + R^3R^4M'Z_2 \rightleftharpoons R^1R^2MZ_2 + R^3R^4M'T_2 \quad (2)$$
$$R_1MT_3 + R^2M'Z_3 \rightleftharpoons R^1MZ_3 + R^2M'T_3 \quad (3)$$
$$2R^1R^2R^3MT + R^4R^5M'Z_2 \rightleftharpoons 2R^1R^2R^3MZ + R^4R^5M'T_2 \quad (4)$$
$$3R^1R^2R^3MT + R^4M'Z_3 \rightleftharpoons 3R^1R^2R^3MZ + R^4M'T_3 \quad (5)$$
$$MT_4 + 2R^1R^2M'Z_2 \rightleftharpoons MZ_4 + 2R^1R^2M'T_2 \quad (6)$$
$$2R^1MT_3 + 3R^2R^3M'Z_2 \rightleftharpoons 2R^1MZ_3 + 3R^2R^3M'T_2 \quad (7)$$

In these equations the exchanging groups are denoted by the symbols T and Z, in accordance with ref. 14. The metals M and M′, as well as the non-exchangeable groups R^1—R^6, may be all the same or different. It is clear that each of the equilibria 2-7 may be considered as a certain sequence of equilibria of type 1.

Besides reactions 1-7, the other equilibria may also exist, e.g.:

$$MT_4 + M'Z_4 \rightleftharpoons MZ_4 + M'T_4$$

However, no experimental data for such equilibria are available.

It is interesting to note that investigations of redistribution reactions of organometallic compounds were initiated by Ladenburg, Friedel and Crafts as early as 1860 [17-19]. Ladenburg was the first who supposed that the variety of reaction products resulting from the interaction of phenyltrichlorosilane with diethylzinc is due to a transfer of phenyl and ethyl groups from one organometallic compound to the other [19].

II. Rationalization of structural effects in redistribution equilibria

1. *General assumptions*

Let us consider organometallic compounds as complexes of anions (and of carbanions), T^- and Z^-, with organometallic cations, R_3M^+. Thus the equilibrium constant, K_{eq}, for reaction 1 may be written as follows:

$$K_{eq} = \frac{[R^1R^2R^3MZ][R^4R^5R^6M'T]}{[R^1R^2R^3MT][R^4R^5R^6M'Z]}$$

$$= \frac{\dfrac{[R^1R^2R^3MZ]}{[R^1R^2R^3M^+][Z^-]} \cdot \dfrac{[R^4R^5R^6M'T]}{[R^4R^5R^6M'^+][T^-]}}{\dfrac{[R^1R^2R^3MT]}{[R^1R^2R^3M^+][T^-]} \cdot \dfrac{[R^4R^5R^6M'Z]}{[R^4R^5R^6M'^+][Z^-]}}$$

$$= \frac{K_m(R^1R^2R^3M^+,Z^-)\cdot K_m(R^4R^5R^6M'^+,T^-)}{K_m(R^1R^2R^3M^+,T^-)\cdot K_m(R^4R^5R^6M'^+,Z^-)} \qquad (8)$$

where $K_m(R^1R^2R^3M^+,Z^-)$ is the equilibrium constant for the formation of $R^1R^2R^3MZ$ from the cation $R^1R^2R^3M^+$ and the anion Z^-, and characterizes the affinity fo Z^- for $R^1R^2R^3M^+$; $K_m(R^4R^5R^6M'^+,T^-)$ is the affinity of anion T^- for the cation $R^4R^5R^6M'^+$; $K_m(R^1R^2R^3M^+,T^-)$ is the affinity of T^- for $R^1R^2R^3M^+$; and $K_m(R^4R^5R^6M'^+,Z^-)$ is the affinity of Z^- for $R^4R^5R^6M'^+$.

The values of K_{eq} for reaction 1 could be calculated, if the formation constants, K_m, were known. However, such calculations are not possible because of the practically complete absence of data on the complexochemical properties of Group IVb organometallic cations (see ref. 20 for a review). Whereas the affinities of anions, especially of carbanions, for organometallic cations are known only for a very limited number of systems, proton affinities are available nowadays for almost all inorganic anions and for many carbanions [21]. The proton affinity of anion X^- is characterized quantitatively by the negative logarithm of the acidic ionization constant, pK_a, of the corresponding acid, HX. The larger the value of $pK_a(HX)$, the higher is the affinity of an anion X^- for the proton.

It was shown in ref. 22 that the affinities of carbanions for the proton and for the methylmercury cation are linearly related:

$$\log K_m(CH_3Hg^+,R^-) = A\cdot pK_a(RH) + \text{const.} \qquad (9)$$

Also, good linear plots exist for the dependence of the proton affinity of many anions and their affinities for cations such as I^+ [23,24], $Ni(H_2O)_6^{2+}$ [25], Cu^{2+} [26], (X-acac)Pd^+ (where X-acac is C-bonded), $Co(NH_3)_5^{2+}$ [27], $[Co(salen)DMF]^+$ and $[\{Co(DO)(DOH)pn\}DMF]^+$ [28]; a linear dependence also exists between the affinities of anions for RHg^+ and RMg^+ [29] cations. These facts suggest that a similar linear dependence could also exist between the proton affinity of anions and their affinities for Group IVb organometallic cations. However, such a dependence cannot be taken for granted because of the present lack of appropriate experimental data.

Nevertheless, we think that equations of type 9 are applicable to all organometallic cations if the nature of the donor atom (e.g. carbon, oxygen, nitrogen) remains the same in series of anions R^- (eqn. 9).

In this paper an attempt will be made to use pK_a values as a measure of the affinity of T^- and Z^- for different organometallic cations, instead of the inaccessible $\log K_m$ values.

It is far more difficult to conceive that eqn. 9 would apply in cases involving, instead of carbanions, any other type of anion X^-, such as halides, O-, S-, N-anions, etc., irrespective of the nature of the donor atom of the anion (eqn. 10):

$$\log K_m(R^iR^jR^kM^+,X^-) = A\cdot pK_a(XH) + \text{const.} \tag{10}$$

where X^- is any anion and M a metal of Group IVb. Of course, eqn. 10 will not be fulfilled in extreme cases of especially large differences in hardness (softness) [30] between the exchangeable anions. However, if one excludes some anions, such as halides and a few others, from consideration, eqn. 10 will be obviously better fulfilled. In this paper we shall try to use eqn. 10 for all anions, never forgetting that this equation is only a very rough approximation.

From eqns. 8 and 10 it follows that:

$$\log K_{eq} = \Delta A(R^1R^2R^3M^+,R^4R^5R^6M'^+)\cdot \Delta pK_a(ZH,TH) \tag{11}$$

where $\Delta A(R^1R^2R^3M^+,R^4R^5R^6M'^+) = A(R^1R^2R^3M^+) - A(R^4R^5R^6M'^+)$ is the difference in the slopes of plots of the affinity of the respective organometallic cation for different anions (T^-, Z^- and others) versus the values pK_a of the conjugate acids of these anions (differentiating factor, DF), and $\Delta pK_a(ZH,TH) = pK_a(ZH) - pK_a(TH)$ is the difference in acidity between ZH and TH (force factor, FF).

Equation 11 involves the two factors which determine equilibrium 1: the difference in the acid strength of ZH and TH and the sensitivity of the complexing properties of the two organometallic cations to a change in the nature of Z^- and T^-. The equilibrium will be shifted to the thermodynamically advantageous side to a greater extent the more FF, i.e. $\Delta pK_a(ZH,TH)$, differs from zero. The differentiating factor, DF, decreases or increases the effect of the force factor. If ΔA and ΔpK_a have the same sign, then $\log K_{eq} > 0$, that is the equilibrium is shifted to the right. If $\Delta pK_a > 0$ and $\Delta A < 0$, then DF will change the direction of action of FF and the equilibrium will be shifted to the left. The latter case occurs in the redistribution of halides between a soft and a hard organometallic cation (vide infra).

2. *The force factor (FF)*

In order to estimate the FF one needs to know the acidities of ZH and TH. Nowadays pK_a values are available for many OH-, SH-, NH- and CH-acids in such solvents as water, benzene, ether, cyclohexylamine, DMSO, DMF etc. (see ref. 21 for a review). However, most of the reactions which will be discussed in this paper were carried out without any solvent. Therefore, it was necessary, first of all, to choose from the available pK_a values those values that corresponded best to such experimental conditions. Because organic compounds of Group IVb are as a rule liquids of low polarity, pK_a values for ZH and TH determined in a non-polar solvent or in the gas phase should be used, because acidities in non-polar solvents are close to acidities in the gas phase [21].

Table 1 lists the pK_a values for some acids in water, DMSO, and DMF solution. The pK_a values used in this paper are given in the last column of Table 1. The pK_a values in DMSO or in DMF, if known, were taken as a measure of the acidity because these values reflect the "proper" acidity of molecules better than those in water. The acidity of HI was estimated by assuming that for the hydrogen halide series the ΔpK_a values are the same between members of the series both in water and in DMF. The acidities of HNCS and HNCO were estimated analogously on the basis of the difference in the pK_a values for HN_3 in water and DMF. The pK_a values for Me_2NH, H_2 and MeSH were estimated from the qualitative order of the molecular acidities in the gas phase [21]:

$$\mathrm{AlkSH} > \mathrm{CH_3NO_2} > \text{cyclo-}\mathrm{C_5H_6} \geqslant \mathrm{CHCl_3} > \mathrm{CH_3OH} > \mathrm{H_2} > \mathrm{NH_3} > \mathrm{CH_4}$$

TABLE 1

ACIDITIES OF SOME H-Hal, NH-, OH-, SH- AND CH-ACIDS

Acid	pK_a			
	In water	In DMSO [33]	In DMF [34]	Used in this paper
H—I	—10 [31]	—	—	1
H—Br	—9.5 [31]	—	1.8	1.8
H—Cl	—7.4 [31]	—	3.4	3.4
H—F	3.2 [31]	—	—	>20 [36]
H—NCS	—0.3 [32]	—	—	~4
H—NCO	3.5 [32]	—	—	7
H—N_3	4.7 [32]	—	8.5	8.5
H—NC	<9.3^a	<12.9	12.0 [35]	<12.9^a
H—NMe_2	—	—	—	35^b
H—OAc	4.7 [32]	11.4	—	11.4
H—OPh	10 [32]	15	—	>15
H—OMe	17 (in MeOH) [32]	27.0	—	27.0
H—OEt	19 (in EtOH) [32]	27.4	—	27.4
H—SMe	—	—	—	16^b
H—CH_3	—	—	—	40^c
H—C_2H_5	—	—	—	42^c
H—H	—	—	—	~30^b
H—CH_2COOR	—	—	24 [35]	24
HC_6F_5	—	—	23 [35]	23

[a] For HCN in water pK_a = 9.3 [32] and in DMSO pK_a = 12.9 [33]. It is assumed that HNC is a stronger acid than HCN. [b] See text. [c] In the MSAD scale by Cram [37].

using, for some members of this series, the pK_a values which have been measured in aprotic solvents [37].

It may be asserted from the sequence given that for CH_3SH p$K_a < 16$, because for CH_3NO_2 p$K_a = 16.9$ [38] (or 15.9 [33]), for cyclopentadiene pK_a = 15.5 [37], and for $CHCl_3$ pK_a = 15.5 [35]. Hydrogen is arranged in the acidity scale between methanol (pK_a = 27, Table 1) and ammonia (pK_a = 35 [37]), therefore for H_2 $27 <$ p$K_a < 35$. The acidity of dimethylamine is obviously intermediate between the acidities of NH_3 and CH_4 (pK_a = 40 [37]*). We take p$K_a \approx 20$ for HF, because in aprotic solvents fluoride ion is a very strong base [36] and can abstract a proton from, for example, the acetonitrile molecule (p$K_a \approx 25$ [37]).

Although the pK_a values given in the last column of Table 1 are arbitrary to a considerable extent, they are nevertheless quite useful for the qualitative or semi-quantitative estimation of FF. AS a matter of fact, for qualitative predictions of a redistribution equilibrium one only needs to know whether FF has a positive or negative sign (as well as DF), and not the absolute value of ΔpK_a(ZH,TH). Then, in principle, one may use the data of any available acidity scale. However, the approximated pK_a values given in Table 1 and referred to an aprotic solvent or to the gas phase allow us in a number of cases to make semi-quantitative calculations of the effects of substituents on relative hardness (or softness) of organometallic cations $R^iR^jR^kM^+$.

3. The differentiating factor (DF)

The differentiating factor depends on the difference in the sensitivities of the K_m values of two organometallic cations taking part in the ligand exchange to a change in the nature of the anions Z^- and T^-. If the two organometallic cations are the same, DF is equal to zero and $K_{eq} = 1$. This is a homo-redistribution reaction; such reactions are not considered in this paper. However, DF may be equal to zero for hetero-redistributions also. In such cases, although two organometallic cations taking part in the ligand exchange are different (e.g. the different central metal atoms), the sensitivities of the K_m values to a change in type of the anions Z^- and T^- is the same for both cations.

For estimating DF we use eqn. 11 in spite of its limited validity, because proton affinities are available for practically all anions.

In Fig. 1 plots are drawn which correspond to the case when $R^1R^2R^3M^+$ is more "soft" and $R^4R^5R^6M'^+$ more "hard" as a Lewis acid than the proton, and Z^- is a stronger base than T^-. The plots are not parallel, that is, they relate to the situation in which DF is not equal to zero. The broken line corresponds to exchange between HZ and HT and has a slope of 45°. Figure 1 shows how K_{eq} can be determined graphically.

Unfortunately, the hardness or softness are not known for most organometallic cations. In order to estimate effects of structural changes in groups bonded to M and M′ and the influence of the nature of M and M′ on the coefficient A in eqn. 11 one must, therefore, make a number of assumptions and compare the results obtained with experimental data.

---

* Besides pK_a = 40 a number of other values of methane acidity have been proposed: pK_a = 47, 48, 50, 57, 58 (see ref. 39 for a review).

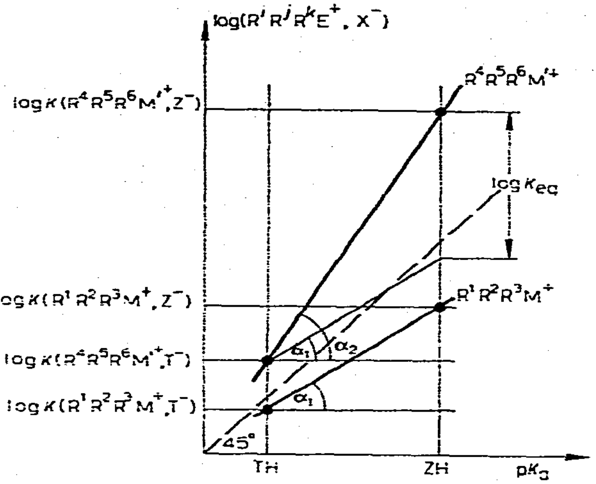


Fig. 1. Plot for the determination of log K_{eq} (see text).

The main assumption is that the sensitivity of K_m to a change in the anion (Z^- and T^-) structures is stronger for "hard" organometallic cations, i.e. $\alpha_2 > \alpha_1$ (Fig. 1). It may be supposed that $A > 1$ in eqn. 11 if the organometallic cation is a harder acid, and $A < 1$, if the cation is a softer acid than the proton.

The second assumption concerns the influence of the nature of non-exchangeable groups R. We suppose that the hardness will be higher for $R^1R^2R^4M^+$ than for $R^1R^2R^3M^+$, if $pK_a(R^4H) < pK_a(R^3H)$. Generally this assumption is confirmed by most of the available experimental data (vide infra).

The differentiating factor will be most evident when the difference in complexing properties between organometallic cations is large. In such a case DF may significantly increase or decrease the effect of FF. Generally, redistribution equilibria are influenced equally strongly both by FF and DF. Equation 11, as follows from the data of Table 2, is fulfilled in most cases so it may be used to predict redistribution equilibria in organometallic systems. However, there are a number of exceptions. If, for instance, the redistribution of halides occurs between a soft and a hard organometallic cation, then eqn. 11 is, as a rule, not fulfilled. This is explained by the fact that in the series of halide anions, F^-, Cl^-, Br^- and I^-, the affinities for the proton and for other hard cations change in an inverse order from that of the affinities for soft Lewis acids. The systems of exchanging halides are discussed in Section IV.

III. The simplest case of redistribution

Reaction 1 is the simplest in stoichiometry and the most studied case of redistributions of organic or inorganic groups in Group IVb organometallic compounds; therefore we consider it first.

The available data are given in Table 2. This table does not include the results of rather numerous studies, in which the investigated systems did not achieve equilibrium or in which the systems changed their phase state during the reaction. The same applies to all the following tables.

(continued on p. 157)

TABLE 2

COMPARISON OF THE EXPERIMENTAL DATA ON EQUILIBRIUM 1 WITH THE RESULTS OBTAINED BY MEANS OF EQUATION 11

No.	M	R^1	R^2	R^3	T	M'	R^4	R^5	R^6	Z	Reaction conditions	Position of equilibrium		
												From eqn. 11	K_{eq} experimental	
1	C	H	H	H	F	C	F	F	F	I		right	right	[44]
2		I	I	I	F		F	F	F	I		left	left	[44]
3		Cl	Cl	Cl	Cl		Br	Br	Br	Br	170°, 7 h, $AlCl_3$	right	right	[45]
4		CH_3	H	Cl	Cl		CH_3	H	Br	Br	80-200°, $AlCl_3$	right	~3.3 ^{a}	[46]
5		H	H	H	$MeCO_2$		CH_3	H	H	$PrCO_2$	80-200°, $AlCl_3$	K_{eq}~1	~0.73 ^{a}	[46]
6	Si	CH_3	CH_3	F	F	Si	CH_3	CH_3	Cl	Cl	70°, 5 h, Et_4NF	right	0.92 ± 0.068	[53]
7		CH_3	CH_3	F	F		CH_3	CH_3	N_3	N_3	25°, 0.2 h	right	1.07 ± 0.05	[53]
8		CH_3	CH_3	F	F		CH_3	CH_3	NCO	NCO	70°; 100 h, $AlCl_3$	right	2.4 ± 0.2	[53]
9		CH_3	CH_3	F	F		CH_3	CH_3	OMe	OMe	70°, 100 h, $AlCl_3$	right	16.2 ± 2.2	[53]
											120°		15.1 ± 1.6	[54]
10		CH_3	CH_3	F	F		CH_3	CH_3	NMe_2	NMe_2	100°, 50 h, $AlCl_3$	right	63 ± 7	[53]
											120°		14.5 ± 2.5	[54]
11		CH_3	CH_3	F	F		CH_3	CH_3	SMe	SMe	120°	right	$(8.2 \pm 1.5) \times 10^{-2}$	[54]
12		C_2H_5	C_2H_5	F	F		C_2H_5	C_2H_5	H	H	100°, 48 h, Bu_4NF	right	2.2×10^{-2}	[56]
13		C_6H_5	C_6H_5	F	F		C_6H_5	CH_3	H	H	20°, 15 h	right	left	[55]
											65°, benzene, Bu_4NF		$(1.4 \pm 0.01) \times 10^{-2}$	[57]
											25°, benzene, Bu_4NF		$(6.6 \pm 0.06) \times 10^{-3}$	[57]
14		CH_3	CH_3	Cl	Cl		CH_3	CH_3	Br	Br	120°, 85 h	right	3.6 ± 0.4	[58, 59]
15		CH_3	CH_3	Cl	Cl		CH_3	CH_3	NCS	NCS	120°, 32 h	right	3.2 ± 0.6	[60]
16		CH_3	CH_3	Cl	Cl		CH_3	CH_3	NCO	NCO	120°, 20 h	right	3.6 ± 0.1	[60]
											370°, 70 h		~4 ^{a}	[61]
17		CH_3	CH_3	Cl	Cl		CH_3	CH_3	N_3	N_3	25°, 1 h	right	11 ± 0.2	[53]
18		CH_3	CH_3	Cl	Cl		CH_3	CH_3	OAc	OAc	120°, 8 days	right	2.9 ± 0.3	[62]
19		CH_3	CH_3	Cl	Cl		CH_3	CH_3	NC	NC	25°, 72 h, benzene	right	4.55 ± 0.2	[60]
											120°		4.6 ± 0.23	[59]
20		CH_3	CH_3	Cl	Cl		CH_3	CH_3	I	I	480°, 5 h	right	~2.5 ^{a}	[61]
21		C_2H_5	C_2H_5	Cl	Cl		C_2H_5	C_2H_5	I	I	400°, 10 h	right	~2.9 ^{a}	[61]
22		CH_3	CH_3	Cl	Cl		CH_3	CH_3	OPh	OPh	150°, 27 days	right	6.25 ± 0.2	[62]
23		CH_3	CH_3	Cl	Cl		CH_3	CH_3	SMe	SMe	120°, 100 h	right	5.6 ± 0.56	[58, 63]

24	Si	CH_3	CH_3	Cl	Cl	Si	CH_3	CH_3	OMe	OMe	120°	right	100 ± 20	[58]
25		CH_3	CH_3	Cl	Cl		CH_3	CH_3	OR	OR		right	right	[64]
26		CH_3	CH_3	Cl	Cl		CH_3	CH_3	H	H	100°, 24 h, Bu_4NCl	right	right	[66]
											100°, Bu_4NCl	right	11.2 ± 1	[65]
27		C_6H_5	CH_3	Cl	Cl		C_6H_5	CH_3	H	H	100°, 96 h	right	~8.7 [a]	[56]
28		CH_3	CH_3	Cl	Cl		CH_3	CH_3	NMe_2	NMe_2	25°, less than 3 min	right	$(6.6 \pm 6.1) \times 10^{-3}$	[58]
29		CH_3	CH_3	Cl	Cl		CH_3	CH_3	CH_3	CH_3	350°, 20 h, $AlCl_3$	right	74.3	[67]
											420°, 15 h, $AlCl_3$		54.9	[67]
											300-400°, $AlCl_3$ p = 54-108 atm.		right	[68]
30		CH_3	CH_3	Br	Br		CH_3	CH_3	I	I	120°, 5 h	right	2.2	[59]
31		CH_3	CH_3	Br	Br		CH_3	CH_3	NCO	NCO	120°, 20 days	right	2.6 ± 0.6	[60]
32		CH_3	CH_3	Br	Br		CH_3	CH_3	NC	NC	120°	right	5.1	[59]
											25°, 18 h		5.25 ± 0.6	[60]
33		CH_3	CH_3	Br	Br		CH_3	CH_3	OPh	OPh	150°, 8 days	right	7.15 ± 0.2	[62]
34		CH_3	CH_3	Br	Br		CH_3	CH_3	SMe	SMe	120°, 46 h	right	22 ± 4	[63]
													30	[58]
35		CH_3	CH_3	Br	Br		CH_3	CH_3	OMe	OMe	120°, 0.5 h	right	155 ± 90	[63]
36		CH_3	CH_3	Br	Br		CH_3	CH_3	NMe_2	NMe_2	120°, 1 h	right	$(2.4 \pm 2.4) \times 10^3$	[62]
											120°, less than 15 h		10^4	[58]
37		CH_3	CH_3	I	I		CH_3	CH_3	SMe	SMe	120°	right	85	[63]
38		CH_3	CH_3	NCO	NCO		CH_3	CH_3	NCS	NCS	25°, 100 h	right	4.5 ± 0.4	[60]
39		CH_3	CH_3	NCO	NCO		CH_3	CH_3	SMe	SMe	120°, 7 days	right	0.22	[62]
40		CH_3	CH_3	NCO	NCO		CH_3	CH_3	OMe	OMe	120°, 20 h	right	17.2 ± 3	[60]
41		CH_3	CH_3	NC	NC		CH_3	CH_3	NCS	NCS	72°, 160 h	right	2.4 ± 0.6	[60]
42		CH_3	CH_3	NC	NC		CH_3	CH_3	SMe	SMe	72°, 100 h	right	71 ± 30	[60]
43		CH_3	CH_3	NC	NC		CH_3	CH_3	NMe_2	NMe_2	72°, 5 days	right	$\sim 1.10^4$	[62]
44		CH_3	CH_3	SMe	SMe		CH_3	CH_3	NCS	NCS	25°, 9 h	right	4.15 ± 0.6	[63]
45		CH_3	CH_3	SMe	SMe		CH_3	CH_3	N_3	N_3	25°, 1 h	right	2.5 ± 0.5	[63]
46		CH_3	CH_3	SMe	SMe		CH_3	CH_3	OAc	OAc	120°, 17 days	right	0.11 ± 0.2	[62]
47		CH_3	CH_3	SMe	SMe		CH_3	CH_3	OMe	OMe	120°, 24 h	right	0.25 ± 0.5	[63]
48		CH_3	CH_3	OMe	OMe		CH_3	CH_3	N_3	N_3	25°, 1 h	right	340 ± 17	[63]
49		CH_3	CH_3	OMe	OMe		CH_3	CH_3	OEt	OEt	150°, 7 days	right	3.5 ± 0.3	[58]
50		CH_3	CH_3	OMe	OMe		CH_3	CH_3	H	H	100°, 96 h, BuLi	right	$\sim 3.6 \times 10^{-2}$	[66]
51		CH_3	CH_3	OMe	OMe		CH_3	CH_3	NMe_2	NMe_2	120°, 40 h	right	4.5 ± 1.2	[58]
52		CH_3	CH_3	NMe_2	NMe_2		CH_3	CH_3	N_3	N_3	25°, 6 h	right	$(3.4 \pm 1) \times 10^3$	[63]

(continued)

TABLE 2 (continued)

No.	M	R^1	R^2	R^3	T	M′	R^4	R^5	R^6	Z	Reaction conditions	Position of equilibrium: From eqn. 11	Position of equilibrium: K_{eq} experimental	
53	Si	CH_3	CH_3	C_2H_5	C_2H_5	Si	CH_3	CH_3	CH_3	CH_3	80°, 120 h, $AlCl_3$	right	~2.8 [a]	[69]
54		H	H	Cl	Cl		H	H	Br	Br	39°, HCl	right	3 ± 0.3	[70]
55		H	H	Cl	Cl		H	H	I	I	39°, HCl	right	6.6 ± 0.6	[70]
											60°, HCl		10 ± 1	[70]
56		H	H	Br	Br		H	H	I	I	39°, HBr	right	2.3 ± 0.05	[70]
											60°, HBr		2.44 ± 0.05	[70]
57		H	H	H	H		H	H	Cl	Cl	100°, 7 days, $AlCl_3$	right	right	[71]
58		H	H	H	H		H	H	C_6H_5	C_6H_5	50-200°, 10 h, H_2PtCl_6	right	right	[72]
59		$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	C_2H_5	C_2H_5		$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	180°, 5 h, $AlCl_3$	right	1.45	[14]
60		C_2H_5	C_2H_5	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$		C_2H_5	C_2H_5	C_2H_5	C_2H_5	180°, 5 h, $AlCl_3$	right	2.2	[14]
61		OMe	OMe	C_6H_5	C_6H_5		OMe	OMe	OMe	OMe	173-204°, 20 h, Na	right	right	[73]
62		Cl	Cl	CH_3	CH_3		Cl	Cl	Cl	Cl	300-400°, $AlCl_3$, p = 24-100 atm.	right	right	[68]
63		Cl	Cl	Cl	Cl		Br	Br	Br	Br	170°, 7 h	right	right	[52]
64		Cl	Cl	Cl	Cl		NCO	NCO	NCO	NCO	135°, 70 h	right	right	[74]
65		Cl	Cl	Cl	Cl		OMe	OMe	OMe	OMe	100°, CCl_4	right	right	[75]
66		CH_3	OMe	OMe	OMe		CH_3	C_6H_5	C_6H_5	C_6H_5	200°, 200 h	right	right	[73]
67		CH_3	Cl	Cl	Cl		CH_3	NMe_2	NMe_2	NMe_2	120°	right	2.5×10^9	[76]
68		CH_3	Cl	Cl	Cl		Cl	CH_3	CH_3	CH_3	350°, 15-20 h, $AlCl_3$	right	40	[14]
69		C_6H_5	H	H	H		H	C_6H_5	C_6H_5	C_6H_5	50-200°, 10 h	right	right	[72]
70		CH_3	F	F	F		CH_3	F	OMe	OMe	120°	right	18.2	[54]
71		CH_3	OMe	OMe	OMe		CH_3	OMe	F	F	120°	right	13.5	[54]
72		CH_3	Cl	Cl	Cl		CH_3	Cl	Br	Br	120°, 39 h	right	2.5 ± 0.2	[77, 78]
73		CH_3	Br	Br	Br		CH_3	Br	Cl	Cl	120°, 39 h	right	2.3 ± 0.1	[77, 78]
74		CH_3	Cl	Cl	Cl		CH_3	Cl	I	I	460°, 0.5 h	right	3.4 ± 0.3 [a]	[61]
75		CH_3	I	I	I		CH_3	I	Cl	Cl	460°, 0.5 h	right	2.2 ± 0.2 [a]	[61]
76		CH_3	Cl	Cl	Cl		CH_3	Cl	OPh	OPh	150°, 163 days	right	4.5 ± 0.09	[14]
77		CH_3	OPh	OPh	OPh		CH_3	OPh	Cl	Cl	150°, 163 days	right	5.5 ± 0.09	[14]
78		CH_3	Cl	Cl	Cl		CH_3	Cl	SMe	SMe	120°, 396 h	right	6.2 ± 0.3	[77]
79		CH_3	SMe	SMe	SMe		CH_3	SMe	Cl	Cl	120°, 396 h	right	15 ± 5	[77]
80		CH_3	Cl	Cl	Cl		CH_3	Cl	OMe	OMe	150°, 19 h	right	24 ± 3.5	[76]
81		CH_3	OMe	OMe	OMe		CH_3	OMe	Cl	Cl	150°, 19 h	right	55 ± 3	[76]

82	Si	CH_3	Cl	Cl	Cl	Si	CH_3	Cl	H	H	100°, Bu_4NCl	right	right	[66]
											100°, 2.3 h, Bu_4NCl		16	[65]
83		CH_3	H	H	H		CH_3	H	Cl	Cl	100°, 2.3 h, Bu_4NCl	right	3.3 ± 0.3	[76]
84		CH_3	Cl	Cl	Cl		CH_3	Cl	NMe_2	NMe_2	20°, 14 days	right	$(2 \pm 3) \times 10^3$	[77]
85		CH_3	NMe_2	NMe_2	NMe_2		CH_3	NMe_2	Cl	Cl	20°, 14 days	right	$(2 \pm 3) \times 10^3$	[77]
86		CH_3	Cl	Cl	Cl		CH_3	Cl	CH_3	CH_3	350°, 20 h, $AlCl_3$	right	39.9	[67]
											420°, 15 h, $AlCl_3$		29.8	[67]
87		CH_3	Br	Br	Br		CH_3	Br	OPh	OPh	150°, 27 days	right	2.6 ± 0.13	[14]
88		CH_3	OPh	OPh	OPh		CH_3	OPh	Br	Br	150°, 27 days	right	3.6 ± 0.22	[14]
89		CH_3	Br	Br	Br		CH_3	SMe	SMe	SMe	120°, 210 h	right	11.5 ± 0.6	[77]
90		CH_3	SMe	SMe	SMe		CH_3	SMe	Br	Br	120°, 210 h	right	14 ± 2	[77]
91		CH_3	Br	Br	Br		CH_3	Br	OMe	OMe	25°, 13 days	right	15.2 ± 0.7	[14]
92		CH_3	OMe	OMe	OMe		CH_3	OMe	Br	Br	25°, 13 days	right	77 ± 7	[14]
93		CH_3	Br	Br	Br		CH_3	Br	NMe_2	NMe_2	120°, 5 h	right	$(7.1 \pm 4.7) \times 10^2$	[77]
94		CH_3	NMe_2	NMe_2	NMe_2		CH_3	NMe_2	Br	Br	20°, 13 days	right	$(6.2 \pm 2) \times 10^3$	[77]
95		CH_3	OMe	OMe	OMe		CH	OMe	OEt	OEt	150°, 7 days	right	3.1 ± 0.1	[76]
96		CH_3	OEt	OEt	OEt		CH_3	OEt	OMe	OMe	150°, 7 days	right	3.8 ± 0.1	[76]
97		CH_3	OMe	OMe	OMe		CH_3	OMe	NMe_2	NMe_2	120°, 3 days	right	3.3 ± 0.4	[76]
98		CH_3	NMe_2	NMe_2	NMe_2		CH_3	NMe_2	OMe	OMe	120°, 3 days	right	2.5 ± 0.3	[76]
99		C_2H_5	Cl	Cl	Cl		C_2H_5	Cl	Br	Br		right	3.6	[14]
100		C_2H_5	Br	Br	Br		C_2H_5	Br	Cl	Cl		right	2.6	[14]
101		C_2H_5	C_6H_5	D	D		D	D	C_6H_5	C_6H_5	130°, 1.3 h	left	left	
102		C_6H_5	CH_3	H	H		H	H	CH_3	C_6H_5	160°, 1 h	left	left	
103		C_6H_5	C_6H_5	CH_3	H		H	CH_3	C_6H_5	C_6H_5	160°, 1 h	left	left	
104		C_6H_5	CH_3	CH_3	H		H	CH_3	CH_3	C_6H_5	160°, 1 h	left	left	[79]
105		$PhCH_2$	CH_3	CH_3	H		H	CH_3	CH_3	$PhCH_2$	160°, 1 h	left	left	
106		C_2H_5	CH_3	CH_3	H		n-C_3H_7	CH_3	CH_3	o-Tol	160°, 1 h	left	left	
107		CH_3	CH_3	H	Cl		CH_3	CH_3	$CH_2{=}CH$	OEt	28.5°	right	1.53	[80]
108		Cl	CH_3	CH_3	CH_3		CH_3	CH_3	CH_3	Cl		left	left	
109		Cl	Cl	CH_3	CH_3		CH_3	CH_3	Cl	Cl	300-400°, 7-15 h	left	left	
110		Cl	Cl	Cl	CH_3		CH_3	Cl	Cl	Cl		left	left	
111		Cl	Cl	CH_3	CH_3		Cl	Cl	Cl	Cl	$AlCl_3$	right	right	[68]
112		Cl	Cl	Cl	CH_3		CH_3	CH_3	Cl	Cl	300-400°, 7-15 h	left	left	
113		Cl	Cl	CH_3	CH_3		CH_3	CH_3	CH_3	Cl	p = 24-108 atm., $AlCl_3$	left	left	
114		CH_3	CH_3	Cl	H		C_6H_5	Cl	Cl	Cl		right	right	
115		CH_3	CH_3	Cl	H		$CF_3CH_2 \cdot CH_2$	Cl	Cl	Cl	100°, 1-24 h	right	right	[66]
116		CH_3	CH_3	Cl	H		CH_3	H	Cl	Cl		right	right	
											100°, 150 h		1.84 ± 0.24	[65]

(continued)

TABLE 2 (continued)

No.	M	R^1	R^2	R^3	T	M′	R^4	R^5	R^6	Z	Reaction conditions	Position of equilibrium: From eqn. 11	Position of equilibrium: K_{eq} experimental	
117	Si	CH_3	CH_3	C_6H_5	H	Si	CH_3	Cl	Cl	Cl	100°, 1-24 h	right	right	[66]
118		CH_3	CH_3	CH_3	H		CH_3	Cl	Cl	Cl	100°, 150 h, Bu_4NCl	right	$(3.8 \pm 3.2) \times 10^3$	[65]
119		C_2H_5	C_2H_5	Cl	Cl		C_6H_5	Cl	Cl	C_2H_5	$AlCl_3$, reflux, 31 h	left	left	[81]
120		C_6H_5	C_6H_5	Cl	Cl		C_6H_5	Cl	Cl	C_6H_5	50-200°, 10 h H_2PtCl_6	left	left	[72]
121		CH_3	H	Cl	Cl		CH_3	Cl	Cl	H		left	left	
122		C_2H_5	H	Cl	Cl		C_2H_5	Cl	Cl	H		left	left	
123		C_6H_5	Cl	Cl	Cl		Cl	Cl	Cl	C_6H_5		left	left	
124		C_2H_5	H	Cl	Cl		C_2H_5	H	H	H		right	right	
125		Cl	H	C_6H_5	C_6H_5		H	Cl	Cl	Cl		right	right	
126		Cl	H	α-Thienyl	α-Tienyl		H	Cl	Cl	Cl		right	right	
127		*p*-Tol	*p*-Tol	*p*-Tol	*p*-Tol		*p*-Tol	*p*-Tol	H	H	240°, 12 h, H_2PtCl_6	right	right	[82]
128		Cl	OMe	OMe	OMe		Cl	Cl	Cl	Cl	100°, CCl_4	right	right	[75]
129		CH_3	CH_3	CH_3	2-Benzothiazolyl		Cl	Cl	Cl	Cl		right	right	[83]
130		CH_3	CH_3	CH_3	2-Benzothiazolyl		CH_3	Cl	Cl	Cl		right	right	
131		CH_3	CH_3	CH_3	2-Benzothiazolyl		CH_3	H	Cl	Cl		right	right	
132		CH_3	CH_3	CH_3	2-Benzothiazolyl		CH_3	CH_3	Cl	Cl		right	right	
133		CH_3	CH_3	CH_3	CH_3		H	Cl	Cl	Cl		right	right	[84]
134		$PhCH_2$-CH_2	CH_3	CH_3	CH_3		H	Cl	Cl	Cl	150-160°, 24 h, H_2PtCl_6	right	right	[84]
135		C_6H_5	CH_3	CH_3	CH_3		H	Cl	Cl	Cl		right	right	
136		n-C_8H_{17}	C_2H_5	C_2H_5	CH_3		H	Cl	Cl	Cl		right	right	
137		n-C_8H_{17}	C_2H_5	C_2H_5	C_2H_5		H	Cl	Cl	Cl		right	right	
138		CH_3	CH_3	CH_3	H		CH_3	CH_3	Cl	Cl	100°, up to 150 h Bu_4NCl	right	26.9 ± 14	[65]
139		CH_3	CH_3	CH_3	H		CH_3	CH_3	H	Cl		right	3.51 ± 1.18	
140		CH_3	CH_3	CH_3	H		CH_3	H	Cl	Cl		right	$(3.6 \pm 6.6) \times 10^2$	
141		CH_3	CH_3	CH_3	H		CH_3	H	H	Cl		right	60.8 ± 40	
142		CH_3	CH_3	H	H		CH_3	Cl	Cl	Cl		right	$(5.08 \pm 3.4) \times 10^2$	
143		CH_3	CH_3	H	H		CH_3	H	Cl	Cl		right	22.3 ± 6.7	

144		CH_3	CH_3	H	H		CH_3	H	H	Cl		right	7.3 ± 2.7	[65]
145		CH_3	CH_3	Cl	H		CH_3	Cl	Cl	Cl	100°, up to 150 h	right	38 ± 21.4	
146		CH_3	CH_3	Cl	H		CH_3	H	H	Cl	Bu_4NCl	left	0.61 ± 0.3	
147		CH_3	CH_3	Cl	Cl		CH_3	H	H	H		right	8.2 ± 10.8	
148	Ge	CH_3	CH_3	Cl	Cl	Ge	CH_3	CH_3	I	I	25°, 2.5 h	right	1.48	[59]
											33°		1.5 ± 0.15	[85]
149		CH_3	CH_3	Cl	Cl		CH_3	CH_3	Br	Br	120°, 27 h	right	3.3 ± 0.2	[85]
150		CH_3	CH_3	Cl	Cl		CH_3	CH_3	NC	NC	72°, 414 h	right	1.7	[59]
151		CH_3	CH_3	Cl	Cl		CH_3	CH_3	OPh	OPh	120°	right	7.1	[85]
152		CH_3	CH_3	Cl	Cl		CH_3	CH_3	SMe	SMe	25°, 100 h	right	18.2 ± 2	[86]
											120°		29.2	[63]
153		CH_3	CH_3	Cl	Cl		CH_3	CH_3	OMe	OMe	25°, 24 h	right	91 ± 40	[63]
154		CH_3	CH_3	Cl	Cl		CH_3	CH_3	OR	OR		right	right	[64]
155		CH_3	CH_3	Cl	Cl		CH_3	CH_3	CH_3	CH_3	300°, many days	right	50 ± 1	[87]
156		CH_3	CH_3	Br	Br		CH_3	CH_3	I	I	120°	right	2.8; 3.8	[85]
											25°, 18 h		2.9 ± 1	[59]
157		CH_3	CH_3	Br	Br		CH_3	CH_3	NC	NC	72°, 100 h	right	2.08	[59]
158		CH_3	CH_3	Br	Br		CH_3	CH_3	OPh	OPh	33°	right	4.2	[85]
159		CH_3	CH_3	Br	Br		CH_3	CH_3	SMe	SMe	25°, 30 h	right	40 ± 15	[85]
160		CH_3	CH_3	Br	Br		CH_3	CH_3	OMe	OMe	25°, 24 h	right	91 ± 9	[85]
161		CH_3	CH_3	I	I		CH_3	CH_3	OPh	OPh	33°	right	0.62	[85]
162		CH_3	CH_3	I	I		CH_3	CH_3	SMe	SMe	25°, 3 h	right	89 ± 8	[63]
											120°, 1 h	right	81	[86]
163		CH_3	CH_3	I	I		CH_3	CH_3	OMe	OMe	25°, 24 h	right	22 ± 7.4	[63]
164		CH_3	CH_3	OMe	OMe		CH_3	CH_3	SMe	SMe	120°, 40 h	right	0.38 ± 0.01	[63]
165		CH_3	Cl	Cl	Cl		CH_3	Cl	Br	Br	20°	right	2.85	[88]
											35°, 1 h		2.5 ± 0.2	[85]
166		CH_3	Br	Br	Br		CH_3	Br	Cl	Cl	20°	right	2.25 ± 0.3	[88]
											35°, 1 h		2.42 ± 0.2	[85]
167		CH_3	Cl	Cl	Cl		CH_3	Cl	I	I	20°	right	1.45 ± 0.15	[88]
											35°, 1 h		1.26 ± 0.1	[85]
168		CH_3	I	I	I		CH_3	I	Cl	Cl	20°	right	1.31 ± 0.1	[88]
											35°		1.39 ± 0.14	[85]
											35°, 1 h		1.39 ± 0.13	[78]
169		CH_3	Cl	Cl	Cl		CH_3	Cl	OPh	OPh	20°	right	7.7 ± 0.6	[88]
											35°, 1 h		7.1 ± 0.7	[85]
170		CH_3	OPh	OPh	OPh		CH_3	OPh	Cl	Cl	20°	right	7.1 ± 6	[88]
											33°		4.2 ± 0.4	[85]
171		CH_3	Cl	Cl	Cl		CH_3	Cl	SMe	SMe	120°, 197 h	right	20.8 ± 2.5	[14]
172		CH_3	SMe	SMe	SMe		CH_3	SMe	Cl	Cl	120°, 197 h	right	25 ± 3	[14]
173		CH_3	Cl	Cl	Cl		CH_3	Cl	OMe	OMe	35°, 20 h	right	47.5 ± 5	[14]
174		CH_3	OMe	OMe	OMe		CH_3	OMe	Cl	Cl	35°, 25 h	right	76 ± 15	[14]
175		CH_3	Br	Br	Br		CH_3	Br	I	I	20°	right	2.5 ± 0.1	[88]
											35°, 1 h		2.4 ± 0.2	[85]

TABLE 2 (continued)

No.	M	R^1	R^2	R^3	T	M′	R^4	R^5	R^6	Z	Reaction conditions	Position of equilibrium: From eqn. 11	Position of equilibrium: K_{eq} experimental
176	Ge	CH_3	I	I	I	Ge	CH_3	I	Br	Br	20°	right	2.45 ± 0.1 [88]
											35°		2.2 ± 0.2 [85, 78]
177		CH_3	Br	Br	Br		CH_3	Br	OPh	OPh	20°	right	4.55 ± 0.8 [88]
											33°		5.9 ± 1 [85]
178		CH_3	OPh	OPh	OPh		CH_3	OPh	Br	Br	20°	right	4.3 ± 4 [88]
											33°		2.7 ± 0.1 [85]
179		CH_3	Br	Br	Br		CH_3	Br	SMe	SMe	33°	right	33 ± 6 [85]
											35°, 4 h		21 ± 4 [78]
180		CH_3	SMe	SMe	SMe		CH_3	SMe	Br	Br	33°	right	35.4 [85]
											35°, 42 h		31 ± 7 [78]
181		CH_3	Br	Br	Br		CH_3	Br	OMe	OMe	33°	right	64 [85]
											35°, 23 h		47 ± 14 [78]
182		CH_3	OMe	OMe	OMe		CH_3	OMe	Br	Br	33°	right	31.4 [85]
											35°, 3 h		25 ± 8.6 [14]
183		CH_3	I	I	I		CH_3	I	OPh	OPh	20°	right	5 ± 3.5 [88]
											33°		1.01 ± 0.05 [85]
184		CH_3	OPh	OPh	OPh		CH_3	OPh	I	I	20°	right	0.81 ± 1 [88]
											33°		0.76 ± 0.07 [88]
185		CH_3	I	I	I		CH_3	I	SMe	SMe	120°, 17.5 h	right	23.2 ± 3.5 [14]
186		CH_3	SMe	SMe	SMe		CH_3	SMe	I	I	120°, 17.5 h	right	30 ± 5 [14]
187		CH_3	Cl	Br	Br		CH_3	Cl	I	I	20°	right	3.2 ± 0.1 [88]
188		CH_3	Cl	Br	Br		CH_3	Cl	OPh	OPh	20°	right	6.2 ± 0.8 [88]
189		CH_3	Cl	I	I		CH_3	Cl	OPh	OPh	20°	right	1.81 ± 0.24 [88]
190		CH_3	Br	I	I		CH_3	Br	OPh	OPh	20°	right	1.81 ± 0.24 [88]
191		F	F	F	F		F	F	Cl	Cl	87°, many h	right	5.3 ± 1 [87]
192		Cl	Cl	Cl	Cl		Cl	Cl	F	F	87°, many h	right	1.95 ± 0.3 [87]
193		OMe	OMe	OMe	OMe		OMe	OMe	Cl	Cl	37°	right	118 ± 15 [87]
194		Cl	Cl	Cl	Cl		Cl	Cl	OMe	OMe	37°	right	20 ± 11 [87]
195		NMe_2	NMe_2	NMe_2	NMe_2		NMe_2	NMe_2	Cl	Cl	37°	right	$(5 \pm 8) \times 10^3$ [87]
196		Cl	Cl	Cl	Cl		Cl	Cl	NMe_2	NMe_2	37°	right	$(1.4 \pm 1) \times 10^3$ [87]
197		Cl	Cl	Cl	Cl		Cl	Cl	Me	Me	300°, many days	right	200 ± 250 [87]
198		NMe_2	NMe_2	NMe_2	NMe_2		NMe_2	NMe_2	OMe	OMe	37°	right	52.5 ± 10 [87]
199		OMe	OMe	OMe	OMe		OMe	OMe	NMe_2	NMe_2	37°	right	2.5 ± 0.3 [87]

200	Ge	F	Cl	Cl	Cl	Ge	Cl	F	F	F	87°, many h	right	2.9 ± 0.9	[87]
201		OMe	Cl	Cl	Cl		Cl	OMe	OMe	OMe	37°, a few min	right	40 ± 9	[87]
202		CH_3	Cl	Cl	Cl		Cl	CH_3	CH_3	CH_3	300°, many days	right	200 ± 280	[87]
203		NMe_2	Cl	Cl	Cl		Cl	NMe_2	NMe_2	NMe_2	37°, a few min	right	$(3.3 \pm 0.8) \times 10^3$	[87]
204		Alk	Cl	Cl	Cl		Cl	Alk	Alk	Alk	200°, 5-20 h, $AlCl_3$	right	right	[50]
205		C_6H_5	Cl	Cl	Cl		Cl	C_6H_5	C_6H_5	C_6H_5	120°, 4 h, $AlCl_3$	right	right	[50]
206		NMe_2	OMe	OMe	OMe		OMe	NMe_2	NMe_2	NMe_2	37°, a few min	right	12.5 ± 1	[87]
207		C_6H_5	C_6H_5	C_6H_5	C_6H_5		C_6H_5	C_6H_5	H	H	300°, 0.5 h	right	right	[14]
208		Alk	Alk	Alk	Alk		Alk′	Alk′	Alk′	Alk′	120-170°, $AlCl_3$	right	right	[89]
209		Alk	Alk	Alk	Alk		Cl	Cl	Cl	Cl	200°, 5-20 h, $AlCl_3$	right	right	[117]
210		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	Cl	Cl	120°, 4-20 h, $AlCl_3$	right	right	[116]
211		C_6H_5	C_6H_5	C_6H_5	C_6H_5		C_6H_5	C_6H_5	Cl	Cl	120°, 4-5 h, $AlCl_3$	right	right	[117]
212	Sn	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	Hal	Hal	Sn	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	H	H	~20°	right	right	[90,91]
213		CH_3	CH_3	Cl	Cl		CH_3	CH_3	OR	OR		right	right	[64]
214		Alk	Alk	Hal	Hal		Alk	Alk	OMe	OMe	fast under boiling	right	right	[92]
215		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	OSO_2R	OSO_2R		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	OMe	OMe		right	right	
216		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	OCOR	OCOR		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	OMe	OMe		right	right	
217		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	CNS	CNS		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	OMe	OMe		right	right	
218		CH_3	CH_3	CH_3	CH_3		$n\text{-}C_4H_9$	Alk	Cl	Cl	0°, 0.5 h	right	right	[93]
219		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	CH_3	CH_3		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	Cl	Cl	140°, 6 h	right	right	[94]
220		C_2H_5	C_2H_5	C_6H_5	C_6H_5		C_2H_5	C_2H_5	Cl	Cl	210°, 3 h	right	right	[94]
221		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	Cl	Cl		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	OAc	OAc		right	right	[95]
222		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	SBu	SBu		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	Cl	Cl		right	right	[96]
223		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	SBu	SBu		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	Br	Br		right	right	[96]
224		Alk	Alk	Alk	Alk		C_6H_5	Cl	Cl	Cl	0°, 20 h	right	right	[93]
225		Alk	Alk	Alk	Alk		$n\text{-}C_4H_9$	Cl	Cl	Cl	200°, 2 h	right	right	[93]
226		C_2H_5	C_2H_5	C_2H_5	C_2H_5		C_2H_5	Cl	Cl	Cl	100°	right	right	[97]
227		C_2H_5	C_2H_5	C_2H_5	C_2H_5		Hal	Hal	Hal	Hal	10-20°, fast	right	right	[97,98]
228		CH_3	CH_3	CH_3	CH_3		Cl	Cl	Cl	Cl	0-37°, fast CCl_4	right	$>10^4$	[99]
229		CH_3	CH_3	CH_3	CH_3		CH_3	CH_3	Cl	Cl	170°, 17 h	right	330	[99]
230		Cl	CH_3	CH_3	CH_3		CH_3	Cl	Cl	Cl	170°, 17 h	right	10^4	[99]
231		Cl	Alk	Alk	Alk		Alk	Cl	Cl	Cl	0-200°, 2 h	right	right	[93,97]
232		Cl	Cl	CH_3	CH_3		Cl	Cl	Cl	Cl	170°, 17 h	right	14	[99]
233		$i\text{-}C_4H_9$	$i\text{-}C_4H_9$	$i\text{-}C_4H_9$	H		C_2H_5	C_2H_5	C_2H_5	D	40°, 30 min	~1	~1	[100]
234		C_6F_5	C_6F_5	C_6F_5	Br		C_2H_5	C_2H_5	C_2H_5	OEt	100°, 3 h, benzene	right	right	
235		C_6F_5	C_6F_5	C_6F_5	Br		C_2H_5	C_2H_5	C_2H_5	$SnEt_3$	100°, 28 h, benzene	right	right	[101]
236		C_6F_5	C_6F_5	C_6F_5	Br		C_2H_5	C_2H_5	C_2H_5	$Sn(C_6F_5)_3$	100°, 4 h, benzene	right	right	[101]

(continued)

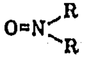
TABLE 2 (continued)

No.	M	R^1	R^2	R^3	T	M'	R^4	R^5	R^6	Z	Reaction conditions	Position of equilibrium		
												From eqn. 11	K_{eq} experimental	
237	Sn	C_2H_5	C_2H_5	C_2H_5	N(Ph)CHO	Sn	CH_3	CH_3	CH_3	H		—	1 (CH); 1.25 (BN)	[102]
238		C_2H_5	C_2H_5	C_2H_5	N(Ph)CHO		C_6H_5	C_6H_5	C_6H_5	H		—	1 (CH)	
239		C_2H_5	C_2H_5	C_2H_5	NPh_2		CH_3	CH_3	CH_3	H		—	1 (CH); $1,2 \times 20^{-2}$ (BN)	
240		C_2H_5	C_2H_5	C_2H_5	PPh_2		CH_3	CH_3	CH_3	H	40° cyclohexane (CH) butyronitril (BN)	—	2,2 (CH); 0,79 (BN)	
241		C_2H_5	C_2H_5	C_2H_5	NEt_2		CH_3	CH_3	CH_3	H		right	1 (CH) $9,2 \times 10^{-2}$ (BN)	
242		C_2H_5	C_2H_5	C_2H_5	OMe		CH_3	CH_3	CH_3	H		left	2,25 (CH) 4,5 (BN)	
243		C_2H_5	C_2H_5	C_2H_5	PPh_2		C_6H_5	C_6H_5	C_6H_5	H		—	0,44 (CH)	
244		C_2H_5	C_2H_5	C_2H_5	OPh		CH_3	CH_3	CH_3	H		left	1 (CH)	
245		C_2H_5	C_2H_5	C_2H_5	OPh		C_6H_5	C_6H_5	C_6H_5	H		left	$2,5 \times 10^{-2}$ (CH)	
246	Pb	CH_3	CH_3	CH_3	CH_3	Pb	CH_3	CH_3	C_2H_5	C_2H_5	80-200°, 1-16 h, $AlCl_3$	right	2,8 ± 0,12	[14]
247		C_2H_5	CH_3	CH_3	CH_3		CH_3	C_2H_5	C_2H_5	C_2H_5		right	2,34 ± 0,12	
248		C_2H_5	C_2H_5	CH_3	CH_3		C_2H_5	C_2H_5	C_2H_5	C_2H_5		right	3,14 ± 0,06	
249		Cl	CH_3	CH_3	CH_3		Cl	CH_3	C_2H_5	C_2H_5		right	3.38	
250		Cl	C_2H_5	CH_3	CH_3		Cl	C_2H_5	C_2H_5	C_2H_5		right	3.28	
251		OAc	OAc	OAc	OAc		OAc	OAc	C_6H_5	C_6H_5	70°, 24 h, HOAc, $Hg(OAc)_2$	right	right	[103]
252		OAc	OAc	OAc	OAc		C_6H_5	C_6H_5	C_6H_5	C_6H_5	70°, 4 h, toluene, $Hg(OAc)_2$	right	right	
253		C_6H_5	C_6H_5	OAc	OAc		C_6H_5	C_6H_5	C_6H_5	C_6H_5	70°, 4 h, toluene, $Hg(OAc)_2$	right	right	
254		C_6H_5	C_6H_5	Cl	Cl		C_6H_5	C_6H_5	C_6H_5	C_6H_5	n-BuOH, boiling, 19 h	right	right	[104]
255		C_6H_5	C_6H_5	C_6H_5	Cl		Cl	C_6H_5	C_6H_5	C_6H_5	n-BuOH, boiling, 6 h	left	left	
256		C_2H_5	C_2H_5	C_2H_5	Cl		Cl	C_2H_5	C_2H_5	C_2H_5	toluene, boiling, 5 h	left	left	
257	Si	Cl	Cl	Cl	Cl	Sn	CH_3	CH_3	CH_3	CH_3	150°, many months	right	right	[99]

258	Si	C_2H_5	C_2H_5	C_2H_5	Hal	Sn	n-C_4H_9	n-C_4H_9	n-C_4H_9	OMe	20-70°	right	right	[64]
259		CH_3	CH_3	CH_3	Hal		n-C_4H_9	n-C_4H_9	n-C_4H_9	OMe		right	right	
260		CH_3	CH_3	CH_3	Hal		n-C_4H_9	n-C_4H_9	n-C_4H_9	OAc		right	right	
261		CH_3	CH_3	Cl	Cl		n-C_4H_9	n-C_4H_9	n-C_4H_9	OAc		right	right	
262		CH_3	CH_3	Cl	Cl		n-C_4H_9	n-C_4H_9	n-C_4H_9	OMe		right	right	
263		C_2H_5	C_2H_5	C_2H_5	F		n-C_4H_9	n-C_4H_9	OMe	OMe		right	right	
264		CH_3	CH_3	CH_3	Hal		n-C_4H_9	n-C_4H_9	OMe	OMe		—	right	
265		CH_3	CH_3	CH_3	Hal		n-C_4H_9	n-C_4H_9	OAc	OAc		—	right	
266		CH_3	CH_3	CH_3	Cl		n-C_4H_9	n-C_4H_9	Cl	OAc	20°	—	right	
267		CH_3	CH_3	CH_3	Cl		n-C_4H_9	n-C_4H_9	n-C_4H_9	C_6H_{10}	N = 0, exothermic	right	right	[108]
268	Si	H	H	H	Cl	Ge	H	H	H	F	TMS, 30°, several h	right	$>10^3$	[106]
269		H	H	H	Br		H	H	H	Cl		right	236 ± 20	
270		H	H	H	I		H	H	H	Br		right	10	
271		H	H	H	I		H	H	H	Cl		right	18700 ± 200	
272		H	H	H	NCO		H	H	H	F	TMS, 20°, several h	right	$>10^3$	
273		H	H	H	NCS		H	H	H	F		right	$>10^3$	
274		H	H	H	N_3		H	H	H	F		right	$>10^3$	
275		CH_3	CH_3	CH_3	R_3P=N—		Alk	Alk	Alk	Hal	exothermic, CH_3Cl	left	right	[107]
276		CH_3	CH_3	CH_3	R_3P=N—		Alk	Alk	Hal	Hal		—	right	
277		CH_3	CH_3	CH_3	R_3P=N—		Alk	Hal	Hal	Hal		—	right	
278	Ge	CH_3	CH_3	CH_3	Br	Sn	C_4H_9	C_4H_9	C_4H_9	OMe	20°	right	right	[64]
279		Hal	Hal	Hal	Hal		n-C_4H_9	n-C_4H_9	n-C_4H_9	n-C_4H_9	160-210°	right	right	[109, 110, 48]
280		Cl	Cl	Cl	Cl		C_2H_5	C_2H_5	C_2H_5	C_2H_5	20°, 170 h	right	right	[109]
281		Cl	Cl	Cl	Cl		CH_3	CH_3	CH_3	CH_3	γ-irradiation (^{60}Co)	right	right	
282		Cl	Cl	Cl	Cl		C_2H_5	C_2H_5	C_2H_5	C_2H_5	150°, 2 h, CH_3NO_2	right	right	[51]
283		n-C_4H_9	n-C_4H_9	n-C_4H_9	n-C_4H_9		Cl	Cl	Cl	Cl	210°, 6 h	—	right	[48]
284		H	Cl	Cl	Cl		CH_3	CH_3	CH_3	CH_3	ehter, 0°	right	right	[105]
285		Alk	Alk	Alk	Alk		Cl	Cl	Cl	Cl	20°, 1 h, CH_3NO_2	—	right	[51]
286		Et	Et	Et	Cl		n-C_4H_9	n-C_4H_9	n-C_4H_9	OBu	50-60°, 1 h	right	right	[111]
287		Hal	Hal	Hal	Hal		n-C_4H_9	n-C_4H_9	n-C_4H_9	CH_2COOMe	60-80°, 4-6 h	right	right	
288		CH_2COO- Me	Cl	Cl	Cl		C_2H_5	C_2H_5	C_2H_5	CH_2COOMe	100°, 3 h	right	right	
289		CH_2COO- Me	CH_2COO- Me	Cl	Cl		C_2H_5	C_2H_5	C_2H_5	CH_2COOMe	120°, 8 h	right	right	
290		MeO	MeO	MeO	Cl		n-C_4H_9	n-C_4H_9	n-C_4H_9	CH_2COOMe	130°, 4 h	right	right	
291		C_2H_5	C_2H_5	C_2H_5	C_2H_5		n-C_4H_9	n-C_4H_9	n-C_4H_9	CH_2COOMe	100°, 2 h	right	right	

(continued)

TABLE 2 (continued)

No.	M	R^1	R^2	R^3	T	M'	R^4	R^5	R^6	Z	Reaction conditions	Position of equilibrium		
												From eqn. 11	K_{eq} experimental	
292	Ge	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	Cl	Sn	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	 $O{=}N\begin{smallmatrix}R\\R\end{smallmatrix}$	1 h	right	right	[112]
293	Ge	Cl	Cl	Cl	Cl	Pb	Alk	Alk	Alk	Alk	100°, 1.5-2 h	right	right	[47]
294		Alk	Cl	Cl	Cl		Cl	Alk	Alk	Alk	140°	—	right	[47]

[a] The values of the equilibrium constants, K_{eq}, were calculated from the composition of the reaction mixtures.

Table 2 contains some purely carbon systems besides organometallic compounds. The pK_a values for prediction of positions of equilibria were taken from Table 1. It was assumed in the determination of the sign of ΔA that the organometallic cation with group R^i which corresponds to a stronger acid R^iH has the larger A. Thus, it was assumed that equilibrium No. 14 (Table 2) is shifted to the right, i.e. $\log K_{eq} = \Delta A(Me_2SiCl^+, Me_2SiBr^+) \cdot \Delta pK_a(HBr, HCl) > 0$, because $\Delta pK_a(HBr, HCl) < 0$ (Table 1) and $A(Me_2SiCl^+) < A(Me_2SiBr^+)$; the latter follows from the fact that HBr is a stronger acid than HCl. The same approach was used in all other examples. When exchange occurred between compounds of two different metals (systems No. 257-294 in Table 2), it was assumed that the metal which is placed higher in Group IVb, i.e., the harder metal cation [40], has the larger value of A. From the 294 systems listed in Table 2, with the help of eqn. 11 and the assumptions above about the nature of the change in A with change in R^i, it was possible to predict correctly the redistribution equilibria in 265 cases.

In 13 systems (No. 237-240, 243, 264-266, 276, 277, 283, 285 and 294; Table 2) it was difficult to estimate the equilibrium; for the first five systems because the pK_a values for compounds such as formanilide, diphenylamine, and diphenylphosphine are unknown, and for the others because it is difficult to predict how the value of the coefficient A will be changed on transfer from Me_3Si^+ to Bu_2SnOMe^+, Bu_2SnOAc^+ and Bu_2SnCl^+, or from Me_3Si^+ to Alk_2GeHal^+, $AlkGeHal_2^+$ etc. Indeed, it is difficult because both the nature of the metals M and M′ and the nature of the non-exchangeable groups bonded to them are different in such reactions.

Only in 16 cases (systems No. 6, 11-13, 39, 46, 47, 50, 126, 161, 164, 184, 241, 242, 244 and 275; Table 2) did eqn. 11 not correspond to the experimental results. In these systems the exchangeable groups are as a rule F, H or SMe. These deviations show that DF depends not only on the pK_a values of the acids (corresponding to the non-exchangeable groups bonded to the metals) but also on other factors which are the subject of discussion in Pearson's concept of "hard and soft acids and bases" [30] (hard acids prefer hard bases and soft acids prefer soft bases).

Most of the data in Table 2 show that the state of a system is thermodynamically preferable when the metal atom of the organometallic compound is bonded to groups of different nature. Statistically, the formation of mixed compounds is always more probable than the formation of simple ones. Also, elementary electrostatic considerations confirm that the formation of mixed compounds is preferable in comparison with the simple ones [41]. However, the prefered formation of mixed compounds contradicts the principle of symbiosis [42]; this principle is not fulfilled, not only in the Group IVb organometallic compounds, but also in series of organomercury compounds (to be published) (see also ref. 43).

IV. Estimation of DF values from experimental data on equilibrium constants of redistributions

1. Comparison of silyl and germyl cations

The data obtained by Cradock and Ebsworth [106] allow one to make a quantitative comparison of A values for the cations H_3Si^+ and H_3Ge^+. The authors studied the following equilibria:

$$H_3MT + HZ \rightleftharpoons H_3MZ + HT \qquad (12)$$

where M = Si or Ge, T = Cl or Br, Z = Br or I and $T \neq Z$.

It should be mentioned that equilibrium 12 is shifted to the left when M = Si and to the right when M = Ge (Table 3). Using the approach given above one may write the following expression for equilibrium 12:

$$\log K_{eq} = \Delta A(H_3M^+,H^+) \cdot \Delta pK_a(ZH,TH) \qquad (13)$$

Since, by definition, $A(H^+) = 1$ (Fig. 1), one may calculate the values of $A(H_3M^+)$ from eqn. 13. The experimental K_{eq} values and the calculated values of $\Delta A(H_3M^+,H^+)$ and $A(H_3M^+)$ are given in Table 3. In each case there are large errors in the calculation of the ΔA values due to a low accuracy both in the determination of the equilibrium constants [106] and in the pK_a values (Table 1). Therefore, in Table 3 the average ΔA values are given from which the average values of $A(H_3M^+)$ were obtained.

The data of Table 3 allow one to calculate DF for the exchange between H_3Si^+ and H_3Ge^+: $\Delta A(H_3Si^+, H_3Ge^+) = 1.7 - (-0.3) = 2.0$.

Cradock and Ebsworth [106] studied also the equilibrium between silyl and germyl halides:

$$H_3SiT + H_3GeZ \rightleftharpoons H_3SiZ + H_3GeT \qquad (14)$$

According to eqn. 11 the equilibrium constant for reaction 14 may be written as follows:

$$\log K_{eq} = \Delta A(H_3Si^+,H_3Ge^+) \cdot \Delta pK_a(ZH,TH) \qquad (15)$$

In Fig. 2 the logarithms of K_{eq} for reaction 14 are plotted vs. the ΔpK_a values for the respective hydrohalide acids ZH and TH. The straight line drawn through the origin of the coordinate system (because $\log K_{eq} = 0$, if $\Delta pK_a = 0$; see eqn. 11) has a slope of 2; this should be the value of $\Delta A(H_3Si^+,H_3Ge^+)$ calculated from the data of Table 3. (The experimental points fall on this straight line rather well (Fig. 2).)

For the germyl cation the value of A is negative. This means that the

TABLE 3

EXPERIMENTAL EQUILIBRIUM CONSTANTS FOR REACTION 12 [106] AND THE VALUES OF ΔA AND A FOR SILYL AND GERMYL CATIONS AS CALCULATED BY MEANS OF EQN. 13

H_3MT	HZ	$\log K_{eq}$ [106]	ΔpK_a (Table 1).	$\Delta A(H_3M^+,H^+)$	$A(H_3M^+)$
H_3SiCl	HBr	−0.05	−1.6	0.03	
H_3SiBr	HI	−1.22	−0.8	1.58	
H_3SiCl	HI	−1.27	−2.4	0.55	
			mean:	$\Delta A = -0.70$	$A(H_3Si^+) = 1.70$
H_3GeCl	HBr	2.86	−1.6	−1.80	
H_3GeBr	HI	0.55	−0.8	−0.69	
H_3GeCl	HI	3.41	−2.4	−1.41	
			mean:	$\Delta A = -1.30$	$A(H_3Ge^+) = -0.30$

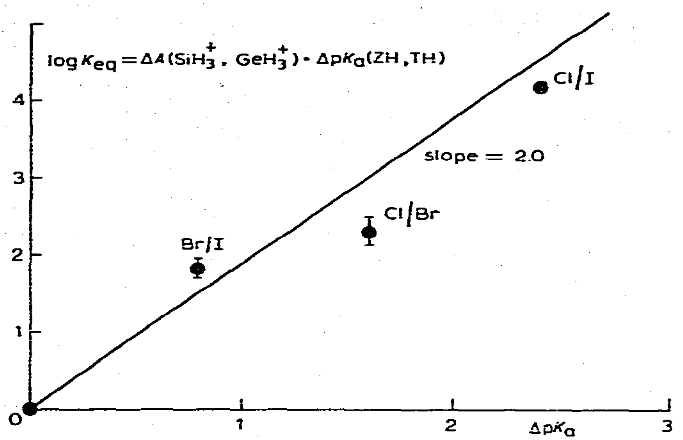


Fig. 2. The dependence of log K_{eq} on ΔK_a(ZH,TH) for reaction 14.

affinities of halide ions for H_3Ge^+ change in the invesre order from that of their affinities for the proton. This conforms to the fact that germanium is a soft Lewis acid [30]. For H_3Si^+ the value of A is positive and larger than 1. This means that the silyl cation is a harder acid than the proton. Thus, the calculated A values may serve as a measure of hardness (softness) of silyl and germyl cations.

2. *Substituent effects on DF in a series of silyl cations*

Most of the quantitative data in Table 2 were obtained at different temperatures. Therefore, they cannot be compared and only a small portion of Table 2 may be used for an estimation of substituent effects on a change in A values.

Moedritzer and Van Wazer [65,76] have determined the equilibrium constants for H/Cl exchange between different organosilicon compounds under identical conditions (systems No. 26, 82, 83, 116, 118 and 138-147; Table 2). Using these equilibrium constants and the approximate pK_a values from Table 1, one can calculate the DF values and their changes on transfer from one organosilicon compound to another. The calculated ΔA values are given in Fig. 3. In this figure the direction of the arrows corresponds to a decrease of the coefficient A in eqn. 10. These data allow one to estimate changes of DF in this series of organosilicon compounds, that is, the relative hardness of the silyl cations. In Table 4 the mean magnitudes of ΔA are given for six silyl cations. As follows from Table 4, the successive substitution of methyl by hydrogen and then of hydrogen by chlorine results in an increase in coefficient A (eqn. 10) of the silyl cation. This is in agreement with the second assumption made in Section II.3 because the sequence of increasing pK_a is $HCl < H_2 < CH_4$ (Table 1). Qualitatively, the same substituent effects on DF may be observed for other silyl cations (Table 2). Table 4 shows that DF may exert the predominant influence on the log K_{eq} values.

It is interesting to compare the equilibria of the same type of redistributions for organosilicon and organogermanium compounds:

$$R_2SiT_2 + R_2SiZ_2 \rightleftharpoons 2R_2SiTZ$$

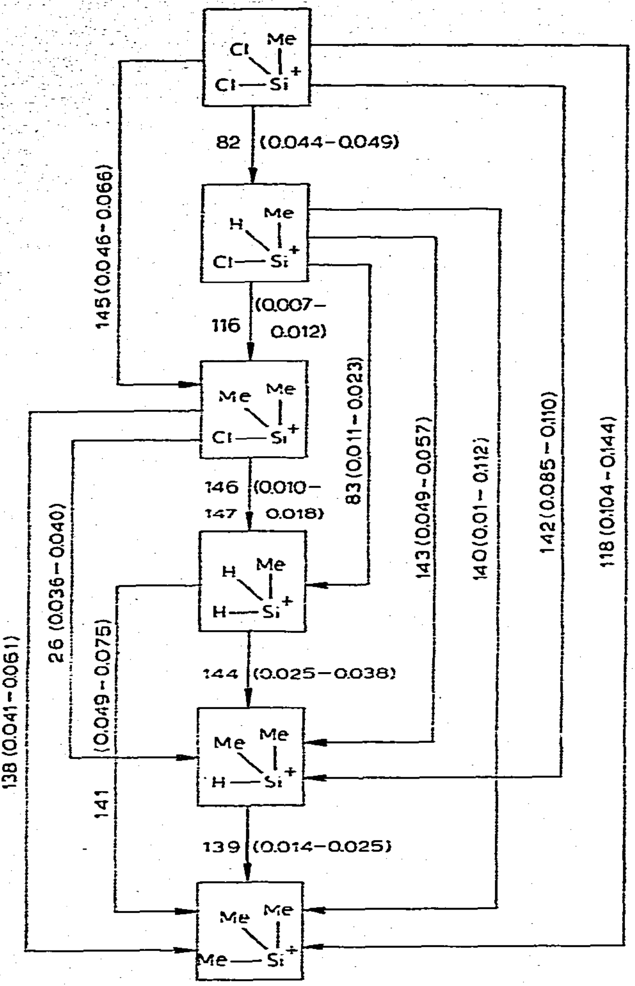


Fig. 3. Effect of substituents bonded to silicon on the DF values (eqn. 11) for reaction of H/Cl exchange in organosilicon compounds. The directions of the arrows correspond to transfer from a more hard to more soft cation. The figures near the arrows correspond to compounds from Table 2. DF(ΔA) values are calculated from the data of refs. 65 and 76 and are given in parentheses.

TABLE 4

THE CALCULATED ΔA VALUES CHARACTERIZING THE RELATIVE HARDNESS OF SIX SILYL CATIONS

No.	Cation	ΔA
1	$CH_3SiCl_2^+$	0.045
2	CH_3SiHCl^+	0.011
3	$(CH_3)_2SiCl^+$	0.008
4	$CH_3SiH_2^+$	0.032
5	$(CH_3)_2SiH^+$	0.020
6	$(CH_3)_3Si^+$	

and

$$R_2GeT_2 + R_2GeZ_2 \rightleftharpoons 2R_2GeTZ$$

(systems No. 14 and 149, 22 and 151, 23 and 152, 24 and 153, 29 and 155, 30 and 156, 32 and 157, 34 and 159, 37 and 162, 47 and 164; Table 2). Such a comparison is given in Fig. 4 from which it follows that the plot of log K_{eq}^{Si} vs. log K_{eq}^{Ge} is linear with a slope close to unity. This means that the dependence of hardness of germyl cations on the nature of the groups bonded to germanium is essentially the same as seen for organosilicon cations.

V. Other redistribution reactions

As mentioned above, eqn. 1 is the simplest case of redistribution in Group IVb organometallic compounds and all other cases of this reaction are a combination of several elementary steps described by eqn. 1. Consequently, for reactions 2-7 the number of items in the equations for log K_{eq} will correspond to the overall stoichiometry of the reaction. Thus, we may write the following equations for reactions 2-7:

for reaction 2:

$$\begin{aligned}\log K_{eq} = {} & \Delta A(R^1R^2ZM^+,R^3R^4ZM'^+)\cdot\Delta pK_a(ZH,TH) + \\ & \Delta A(R^1R^2TM^+,R^3R^4TM'^+)\cdot\Delta pK_a(ZH,TH)\end{aligned} \qquad (16)$$

for reaction 3:

$$\begin{aligned}\log K_{eq} = {} & \Delta A(R^1Z_2M^+,R^1Z_2M'^+)\cdot\Delta pK_a(ZH,TH) + \\ & \Delta A(R^2T_2M^+,R^1T_2M'^+)\cdot\Delta pK_a(ZH,TH) + \\ & \Delta A(R^1TZM^+,R^1TZM'^+)\cdot\Delta pK_a(ZH,TH)\end{aligned} \qquad (17)$$

(continued on p. 167)

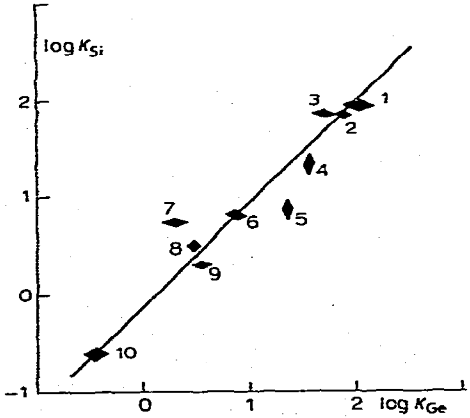


Fig. 4. The dependence between logs of equilibrium constants for redistribution reactions between similar organo-silicon and -germanium compounds (from the data of refs. 58, 59, 62, 63, 67, 85-87). The numbers of the points correspond to the following pairs of systems from Table 2: 1—(24 and 153); 2—(37 and 162); 3—(29 and 155); 4—(34 and 159); 5—(23 and 152); 6—(22 and 151); 7—(32 and 157); 8—(14 and 149); 9—(30 and 156); 10—(47 and 164).

TABLE 5

COMPARISON OF EXPERIMENTAL EQUILIBRIA OF REACTION 2 WITH THOSE CALCULATED FROM EQN. 16

No.	M	R^1	R^2	T	M′	R^3	R^4	Z	Reaction conditions	Position of equilibrium		
										From eqn. 16	K_{eq} experimental	
1	C	H	H	H	C	F	F	F		right	left	[44]
2	Si	C_2H_5	C_2H_5	C_2H_5	Si	n-C_3H_7	n-C_3H_7	n-C_3H_7	180°, 5 h, $AlCl_3$	right	right	[46]
3		I	I	I		F	F	F	700°	right	right	[113]
4		H	H	H		F	F	F	0-20°, 2 years (!)	right	left	[114]
5		CH_3	CH_3	H		CH_3	Cl	Cl	100°, Bu_4NCl	right	1.2×10^3	[65]
6		CH_3	CH_3	H		CH_3	H	Cl	100°, Bu_4NCl	right	18.7 ± 7.7	[65]
7	Ge	Alk	Alk	Alk	Ge	Alk	Alk	Alk	170°, $AlCl_3$	right	right	[89]
8		Alk	Alk	Alk		Cl	Cl	Cl	200°, 5-20 h, $AlCl_3$	right	right	[49,50]
9	Sn	CH_3	CH_3	CH_3	Sn	C_2H_5	C_2H_5	C_2H_5	60°, 5 h, $AlCl_3$, pentane	right	right	[46, 16]
10		Cl	Cl	Cl		C_2H_5	C_2H_5	Alk	0°, 0.5 h, CH_2Cl_2	right	right	[52]
11		Cl	Cl	Cl		C_6H_5	C_6H_5	C_6H_5	180°	right	right	[52]
12		Cl	Cl	Cl		p-Tol	p-Tol	p-Tol		right	right	[52]
13		Hal	Hal	Hal		Alk	Alk	Alk	200°, 10-15 h	right	right	[97, 98, 115]
14		OAc	OAc	OAc		Alk	Alk	Alk	200°, 10 h	right	right	[115]

15	Pb	CH_3	CH_3	CH_3	Pb	Alk	Alk	Alk	80-200°, 1-16 h, $AlCl_3$	right	right	[46]
16		C_2H_5	C_6H_5	C_6H_5		OAc	OAc	OAc	70°, 4 h, AcOH, $Hg(OAc)_2$	right	right	[103]
17	Si	CH_3	CH_3	Cl	Ge	CH_3	CH_3	Br	120°	left	$(2.9 \pm 1.2) \times 10^{-4}$	[59]
18		CH_3	CH_3	Cl		CH_3	CH_3	NC	120°	right	$(6.7 \pm 1) \times 10^{-2}$	[59]
19		CH_3	CH_3	Cl		CH_3	CH_3	SMe	120°	right	$(1.02 \pm 0.3) \times 10^{-3}$	[63]
20		CH_3	CH_3	Cl		CH_3	CH_3	OMe	120°	right	$(4.5 \pm 1.6) \times 10^{4}$	[63]
21		CH_3	CH_3	Br		CH_3	CH_3	NC	120°	right	$(2.6 \pm 1) \times 10^{2}$	[59]
22		CH_3	CH_3	Br		CH_3	CH_3	SMe	120°	right	4.45 ± 0.5	[63]
23		CH_3	CH_3	Br		CH_3	CH_3	OMe	120°	right	$(9.2 \pm 5.4) \times 10^{12}$	[63]
24		CH_3	CH_3	I		CH_3	CH_3	Cl	120°	right	$(8.3 \pm 1.9) \times 10^{5}$	[59]
25		CH_3	CH_3	I		CH_3	CH_3	Br	120°	right	$(5.0 \pm 0.9) \times 10^{3}$	[59]
26		CH_3	CH_3	I		CH_3	CH_3	SMe	120°	right	$(3.5 \pm 0.5) \times 10^{4}$	[63]
27		CH_3	CH_3	I		CH_3	CH_3	OMe	120°	right	$(1.1 \pm 0.2) \times 10^{10}$	[63]
28		CH_3	CH_3	OMe		CH_3	CH_3	SMe	120°	left	$(2.6 \pm 0.5) \times 10^{4}$	[63]
29	Ge	Br	Br	Br	Sn	Alk	Alk	Alk	250°	right	right	[110]
30		Br	Br	Br		C_6H_5	C_6H_5	C_6H_5		right	right	
31		I	I	I		Alk	Alk	Alk		right	right	
32		I	I	I		C_6H_5	C_6H_5	C_6H_5		right	right	
33	Sn	Alk	Alk	Ar	Pb	OAc	OAc	OAc	50°, AcOH, $Hg(OAc)_2$, boiling in CH_3OH	—	right	[116]
34		C_2H_5	C_2H_5	Ar		$EtCO_2$	$EtCO_2$	$EtCO_2$		—	right	[116]

TABLE 6

COMPARISON OF EXPERIMENTAL EQUILIBRIA OF REACTION 3 WITH THOSE CALCULATED FROM EQN. 17

No.	M	R^1	T	M′	R^2	Z	Reaction conditions	Position of equilibrium		
								From eqn. 17	K_{eq} experimental	
1	Si	CH_3	Cl	Ge	CH_3	I	120°, many days	left	$(1.5 \pm 0.7) \times 10^{-12}$	[78]
2		CH_3	Cl		CH_3	Br	120°, many days	left	$(9.7 \pm 4) \times 10^{-6}$	[78]
3		CH_3	Cl		CH_3	SMe		right	$(1.4 \pm 0.6) \times 10^{-7}$	[14]
4		CH_3	Cl		CH_3	OMe		right	$(1 \pm 10) \times 10^{14}$	[14]
5		CH_3	Cl		CH_3	NMe_2		right	$(3.5 \pm 3) \times 10^{12}$	[14]
6		CH_3	Br		CH_3	I	120°, many days	left	$(4.2 \pm 1) \times 10^{-5}$	[78]
7		CH_3	Br		CH_3	SMe		right	6.3 ± 1.5	[14]
8		CH_3	Br		CH_3	OMe		right	$(1 \pm 10) \times 10^{20}$	[14]
9		CH_3	Br		CH_3	NMe_2		right	$(4.0 \pm 3.4) \times 10^{20}$	[14]
10		CH_3	I		CH_3	SMe		right	$(9.1 \pm 4.1) \times 10^{8}$	[14]
11		CH_3	I		CH_3	NMe_2		right	$(4.2 \pm 8.6) \times 10^{28}$	[14]

TABLE 7

COMPARISON OF EXPERIMENTAL EQUILIBRIA OF REACTION 4 WITH THOSE CALCULATED FROM EQN. 18

No.	M	R^1	R^2	R^3	T	M′	R^4	R^5	Z	Reaction conditions	Position of equilibrium		
											From eqn. 18	Experimental	
1	Si	CH_3	CH_3	CH_3	F	Si	CH_3	CH_3	OMe	120°	left	$(4.5 \pm 0.8) \times 10^{-2}$	[54]
2		CH_3	CH_3	CH_3	F		CH_3	CH_3	NMe_2	120°	left	$(3.6 \pm 1.1) \times 10^{-2}$	[54]
3		CH_3	CH_3	CH_3	F		CH_3	CH_3	H		left	$(8.1 \pm 6.4) \times 10^{-1}$ [a]	[54]
4		CH_3	CH_3	CH_3	F		CH_3	CH_3	SMe	120°	right	1.7 ± 0.8	[54]
5		CH_3	CH_3	CH_3	F		CH_3	CH_3	Cl	120°	right	$(1.2 \pm 0.2) \times 10^{2}$	[54]
6		CH_3	CH_3	CH_3	F		CH_3	CH_3	Br		right	$(2.8 \pm 0.7) \times 10^{2}$ [a]	[54]
7		CH_3	CH_3	CH_3	Cl		CH_3	CH_3	OMe	120°, 17 h	left	$(5.3 \pm 1.7) \times 10^{-4}$	[54]
8		CH_3	CH_3	CH_3	Cl		CH_3	CH_3	NMe_2	25°, 10 days	left	$(8 \pm 3.3) \times 10^{-4}$	[58]

9		CH_3	CH_3	CH_3	Cl		CH_3	CH_3	H	100°	left	(5.6 ± 3.4) × 10^{-3}	[14]
10		C_2H_5	C_2H_5	C_2H_5	H		C_2H_5	C_2H_5	Cl	distillation in the presence of $AlCl_3$	right	right	[81]
11		CH_3	CH_3	CH_3	Cl		CH_3	CH_3	SMe	120°, 137 h	left	(9.8 ± 1.8) × 10^{-3}	[58]
12		CH_3	CH_3	CH_3	Cl		CH_3	CH_3	Br	120°, 16 h	right	2.5 ± 0.2	[58]
13		CH_3	CH_3	CH_3	Br		CH_3	CH_3	NMe_2	25°, 2 h	left	(4.2 ± 0.2) × 10^{-4}	[58]
14		CH_3	CH_3	CH_3	Br		CH_3	CH_3	Me	120°, 45 h	left	(4.2 ± 0.2) × 10^{-4}	[58]
15	Ge	C_6H_5	C_6H_5	C_6H_5	C_6H_5	Ge	C_6H_5	Cl	Cl	140°, 15 h, $AlCl_3$	right	right	[47]
16		C_6H_5	C_6H_5	C_6H_5	C_6H_5		Cl	Cl	Cl	120°, 4 h, $AlCl_3$	right	right	[50]
17		Cl	Cl	Cl	Cl		C_6H_5	C_6H_5	C_6H_5	125°, 6 h, $AlCl_3$	right	right	[50]
18		Alk	Alk	Alk	Alk		Cl	Cl	Cl	200°, 5-20 h, $AlCl_3$	right	right	[50]
19		Cl	n-C_4H_9	n-C_4H_9	n-C_4H_9		Cl	Cl	Cl	200°, 5 h, $AlCl_3$	right	right	[50]
20	Sn	C_2H_5	C_6H_5	C_6H_5	C_6H_5	Sn	C_6H_5	Cl	Cl	210°, 4.5 h	right	right	[94]
21		n-C_4H_9	C_6H_5	C_6H_5	C_6H_5		n-C_4H_9	Cl	Cl		right	right	
22		n-C_4H_9	Cl	Cl	Cl		CH_3	CH_3	CH_3	180°, 2 h	right	right	[93]
23		CH_3	CH_3	CH_3	CH_3		n-C_4H_9	Cl	Cl	80°, 3 h	right	right	
24		Hal	Hal	Hal	Hal		Alk	Alk	Alk	100°, 15 h	right	right	[97]
25	Pb	C_6H_5	OAc	OAc	OAc	Pb	C_6H_5	C_6H_5	C_6H_5	70°, 2 h, AcOH, $Hg(OAc)_2$	right	right	[103]
26		C_6H_5	C_6H_5	C_6H_5	C_6H_5		C_6H_5	OAc	OAc	70°, 40 h, AcOH, $Hg(OAc)_2$	right	right	
27	Sn	C_2H_5	C_2H_5	C_2H_5	CH_2CO_2- Ge Me		Hal	Hal	Hal	60-130°, 2-8 h	right	right	[111]

---

[a] The values of the equilibrium constants in ref. [54] were calculated from the data of ref. 14.

TABLE 8

COMPARISON OF EXPERIMENTAL EQUILIBRIA OF REACTION 5 WITH THOSE CALCULATED FROM EQN. 19

No.	M	R^1	R^2	R^3	T	M′	R^4	Z	Reaction conditions	Position of equilibrium		
										From eqn. 19	K_{eq} experimental	
1	Si	CH_3	CH_3	CH_3	F	Si	CH_3	OMe	120°	left	$(3.7 \pm 1.8) \times 10^{-5}$	[54]
2		CH_3	CH_3	CH_3	F		CH_3	NMe_2		left	$(3.6 \pm 2.4) \times 10^{-3}$ [a]	[54]
3		CH_3	CH_3	CH_3	F		CH_3	H		left	$(3.0 \pm 4.2) \times 10^{-3}$ [a]	[54]
4		CH_3	CH_3	CH_3	F		CH_3	SMe		right	$(8.0 \pm 6.9) \times 10^{-2}$ [a]	[54]
5		CH_3	CH_3	CH_3	F		CH_3	Cl	120°	right	$(1.3 \pm 0.6) \times 10^{5}$	[14]
6		CH_3	CH_3	CH_3	F		CH_3	Br		right	$(1.2 \pm 0.7) \times 10^{6}$ [a]	[54]
7		CH_3	CH_3	CH_3	Cl		CH_3	OMe		left	$(7 \pm 2.7) \times 10^{-9}$	[77]
8		CH_3	CH_3	CH_3	Cl		CH_3	NMe_2	25°, 14 days	left	$(1.2 \pm 0.2) \times 10^{-10}$	[77]
9		CH_3	CH_3	CH_3	Cl		CH_3	H	100°	left	$(1.0 \pm 0.9) \times 10^{-8}$	[28]
10		CH_3	CH_3	CH_3	Cl		CH_3	SMe	120°	left	$(6.7 \pm 2.4) \times 10^{-7}$	[77]
11		CH_3	CH_3	CH_3	Cl		CH_3	Br	120°	right	10.32 ± 1.4	[77]
12		CH_3	CH_3	CH_3	Br		CH_3	NMe_2	25°, 13 days	left	$(6 \pm 1.6) \times 10^{-12}$	[77]
13		CH_3	CH_3	CH_3	Br		CH_3	SMe	120°, 210 h	left	$(3.5 \pm 2.6) \times 10^{-6}$	[77]
14		C_6H_5	C_6H_5	C_6H_5	C_6H_5		Cl	Cl	170°, 19 h, $AlCl_3$	right	right	[47]
15	Ge	Cl	Cl	Cl	Cl	Ge	C_6H_5	C_6H_5	170°, 19 h, $AlCl_3$	—	right	[47]
16	Pb	OAc	OAc	OAc	OAc	Pb	C_6H_7	C_6H_7	70°, 24 h, AcOH, $Hg(OAc)_2$	right	right	[103]
17	Sn	C_2H_5	C_2H_5	C_2H_5	CH_2CO_2-Me	Ge	Cl	Cl	130°, 8 h	right	right	[111]

---

[a] The values of the equilibrium constants in ref. 54 were calculated from the data of ref. 14.

for reaction 4:

$$\begin{aligned}\log K_{\mathrm{eq}} = {} & \Delta A(\mathrm{R^1R^2R^3M^+,R^4R^5TM'^+})\cdot\Delta \mathrm{p}K_{\mathrm{a}}(\mathrm{ZH,TH}) + \\ & \Delta A(\mathrm{R^1R^2R^3M^+,R^4R^5ZM'^+})\cdot\Delta \mathrm{p}K_{\mathrm{a}}(\mathrm{ZH,TH}) \qquad (18)\end{aligned}$$

for reaction 5:

$$\begin{aligned}\log K_{\mathrm{eq}} = {} & \Delta A(\mathrm{R^1R^2R^3M^+,R^4T_2M'^+})\cdot\Delta \mathrm{p}K_{\mathrm{a}}(\mathrm{ZH,TH}) + \\ & \Delta A(\mathrm{R^1R^2R^3M^+,R^4Z_2M'^+})\cdot\Delta \mathrm{p}K_{\mathrm{a}}(\mathrm{ZH,TH}) + \\ & \Delta A(\mathrm{R^1R^2R^3M^+,R^4ZTM'^+})\cdot\Delta \mathrm{p}K_{\mathrm{a}}(\mathrm{ZH,TH}) \qquad (19)\end{aligned}$$

for reaction 6:

$$\begin{aligned}\log K_{\mathrm{eq}} = {} & \Delta A(\mathrm{Z_3M^+,R^1R^2ZM'^+})\cdot\Delta \mathrm{p}K_{\mathrm{a}}(\mathrm{ZH,TH}) + \\ & \Delta A(\mathrm{T_3M^+,R^1R^2ZM'^+})\cdot\Delta \mathrm{p}K_{\mathrm{a}}(\mathrm{ZH,TH}) + \\ & \Delta A(\mathrm{TZ_2M^+,R^1R^2ZM'^+})\cdot\Delta \mathrm{p}K_{\mathrm{a}}(\mathrm{ZH,TH}) + \\ & \Delta A(\mathrm{T_2ZM^+,R^1R^2TM'^+})\cdot\Delta \mathrm{p}K_{\mathrm{a}}(\mathrm{ZH,TH}) \qquad (20)\end{aligned}$$

for reaction 7:

$$\begin{aligned}\log K_{\mathrm{eq}} = {} & \Delta A(\mathrm{R^1TZM^+,R^2R^3TM'^+})\cdot\Delta \mathrm{p}K_{\mathrm{a}}(\mathrm{ZH,TH}) + \\ & \Delta A(\mathrm{R^1TZM^+,R^2R^3ZM'^+})\cdot\Delta \mathrm{p}K_{\mathrm{a}}(\mathrm{ZH,TH}) + \\ & 2\Delta A(\mathrm{R^1Z_2M^+,R^2R^3ZM'^+})\cdot\Delta \mathrm{p}K_{\mathrm{a}}(\mathrm{ZH,TH}) + \\ & 2\Delta A(\mathrm{R^1T_2M^+,R^2R^3TM'^+})\cdot\Delta \mathrm{p}K_{\mathrm{a}}(\mathrm{ZH,TH}) \qquad (21)\end{aligned}$$

Experimental data available for reactions 2-7 are given in Tables 5-10 which show that most of the data are in agreement with predictions based on eqns. 16-21 and the assumptions made in Section II.3. However, Tables 5-10 include also some reactions in which the experimental position of the equilibria does not correspond to that calculated from eqns. 16-21. And again, as in Table 2, the deviations are observed in the cases where one of the exchangeable groups is F, H, SMe, CN or I (systems No. 1, 4, 18, 19, 28 in Table 5; No. 3 in Table 6; No. 4 in Table 8; No. 3, 14, 15, 17 in Table 10). These facts indicate that the affinity of organometallic cations for the exchangeable groups, T and Z, is not always determined only by the pK_{a} values of the non-exchangeable groups, R, bonded to the central metal atom. Generally, the pK_{a} values of RH should be used only as the first step in the prediction of the equilibrium of the redistribution reactions, especially if T or Z are halides or some other extremely soft or extremely hard anions.

TABLE 9

COMPARISON OF EXPERIMENTAL EQUILIBRIA OF REACTION 6 WITH THOSE CALCULATED FROM EQN. 20

No.	M	T	M'	R¹	R²	Z	Reaction conditions	Position of equilibrium		
								From eqn. 20	Experimental	
1	Ge	Br	Sn	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	OAc	boiling in benzene	right	right	[117]
2		Br		$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	$EtCO_2$		right	right	

TABLE 10

COMPARISON OF EXPERIMENTAL EQUILIBRIA OF REACTION 7 WITH THOSE CALCULATED FROM EQN. 21

No.	M	R^1	T	M′	R^2	R^3	Z	Reaction conditions	Position of equilibrium		
									From eqn. 21	K_{eq} experimental	
1	Si	CH_3	F	Si	CH_3	CH_3	Cl	120°	left	$(7.1 \pm 4.6) \times 10^{-3}$	[14]
2		CH_3	F		CH_3	CH_3	Br		left	$(1.25 \pm 1) \times 10^{-5}$ [a]	[54]
3		CH_3	F		CH_3	CH_3	SMe		left	14 ± 10 [a]	[54]
4		CH_3	F		CH_3	CH_3	OMe	120°	right	$(3.6 \pm 3.7) \times 10^{3}$	[54]
5		CH_3	F		CH_3	CH_3	H		right	$(3.2 \pm 4) \times 10^{2}$ [a]	[54]
6		CH_3	F		CH_3	CH_3	NMe_2		right	47 ± 50 [a]	[54]
7		CH_3	Cl		CH_3	CH_3	Br	120°	left	0.17 ± 0.02	[14]
8		CH_3	Cl		CH_3	CH_3	SMe	120°	right	$(2 \pm 0.4) \times 10^{5}$	[14]
9		CH_3	Cl		CH_3	CH_3	OMe	120°	right	$(1 \pm 0.5) \times 10^{8}$	[14]
10		CH_3	Cl		CH_3	CH_3	H	100°	right	$(1 \pm 0.6) \times 10^{7}$	[14]
11		CH_3	Cl		CH_3	CH_3	NMe_2	25°	right	$(4.7 \pm 2.9) \times 10^{7}$	[14]
12		CH_3	Br		CH_3	CH_3	SMe	120°	right	$(6.7 \pm 0.7) \times 10^{5}$	[14]
13		CH_3	Br		CH_3	CH_3	NMe_2	120°	right	$(1 \pm 0.2) \times 10^{11}$	[14]
14	Ge	CH_3	Cl	Ge	CH_3	CH_3	I	120°	left	1.73×10^{3}	[85]
15		CH_3	Cl		CH_3	CH_3	Br	120°	left	5.92 ± 0.42	[85]
16		CH_3	Cl		CH_3	CH_3	OPh	120°	right	$(7.1 \pm 1) \times 10^{5}$	[85]
17		CH_3	Br		CH_3	CH_3	I	120°	left	3.39×10^{2}	[85]
18		CH_3	Br		CH_3	CH_3	OPh	120°	right	1.89×10^{5}	[85]
19		CH_3	Br		CH_3	CH_3	SMe	120°	right	5.03×10^{8}	[85]
20		CH_3	Br		CH_3	CH_3	OMe	120°	right	2.09×10^{9}	[85]
21		CH_3	I		CH_3	CH_3	OPh	120°	right	1.48×10^{2}	[85]

[a] The values of the equilibrium constants in ref. 54 were calculated from the data of ref. 14.

VI. Conclusions

The proposed approach to an explanation of the redistribution equilibria in the Group IVb organometallic compounds is, in our opinion, rather useful. The equilibrium may be predicted best, if the formation constants of complexes of organometallic cations with different anions are known, but such data are not available at present for the Group IVb organometallic cations. Therefore, instead of the unknown formation constants, we propose to use the pK_a values of exchangeable anions and non-exchangeable groups for a prediction of the equilibrium position. Most (93%) of the data of Tables 2-10 may be explained on the basis of this approach.

In general the redistribution equilibria are influenced not only by differences in the pK_a values of the exchangeable groups T and Z (force factor) but also by a differentiating factor. The effect of DF is especially strong in the exchange of halides and some other groups, e.g., SMe. Thus, the affinity of the germyl cation, GeH_3^+, to halides changes in the inverse order from that of the pK_a values of hydrohalic acids.

Finally, it should be noted that the approach proposed may be applied to equilibria in which organometallic compounds of all other Groups of the Periodic Table participate.

References

1 K.A. Kocheshkov, N.I. Zemlyansky, N.N. Sheverdina and E.M. Panov, Metodi elementoorganicheskoi khimii, Germanii, olovo, svinets, Nauka, Moscow, 1968.
2 L.N. Makarova and A.N. Nesmeyanov, Metodi elementoorganicheskoi khimii, Rtut', Nauka, Moscow, 1965.
3 A.N. Nesmeyanov and R.A. Sokolik, Metodi elementoorganicheskoi khimii; Bor, aluminii, gallii, indii, tallii, Nauka, Moscow, 1964.
4 D. Seyferth, J. Organometal. Chem., 62 (1973) 19.
5 M.H. Abraham and P.L. Grellier, J. Chem. Soc., Perkin Trans. II, (1973) 1132.
6 R.C. Larock and H.C. Brown, J. Organometal. Chem., 26 (1971) 35.
7 G. Calingaert and H.A. Beatty, in H. Gilman (Ed.), Organic Chemistry. An Advanced Treatise, Vol. II, Wiley, New York, 1950, p. 1806.
8 J.R. Van Wazer, Amer. Sci., 50 (1962) 450.
9 J.R. Van Wazer and L.C.D. Groenweghe, NMR in Chemistry, Academic Press, New York, 1965, p. 283.
10 R.E. Dessy, T. Psarras and S. Green, Ann. N.Y. Acad. Sci., 125 (1965) 43.
11 J.C. Lockhart, Chem. Rev., 65 (1965) 131.
12 K. Moedritzer, Organometal. Chem. Rev., 1 (1966) 179.
13 J.R. Van Wazer and K. Moedritzer, Angew. Chem., 78 (1966) 401.
14 K. Moedritzer, Advan. Organometal. Chem., 6 (1968) 171.
15 O.A. Reutov, I.P. Beletskaya and V.I. Sokolov, Mekhanismi reactsii metalloorganicheskikh soedinenii, Khimia, Moscow, 1972.
16 J.R. Van Wazer, Ann. N.Y. Acad. Sci., 159 (1969) 5.
17 C. Friedel and J.-M. Crafts, Ann. Chim. Phys., 9 (1866) 5.
18 C. Friedel and A. Ladenburg, Ann., 143 (1867) 124.
19 A. Ladenburg, Ber., 7 (1874) 387.
20 I.P. Beletskaya, K.P. Butin, A.N. Ryabtsev and O.A. Reutov, J. Organometal. Chem., 59 (1973) 1.
21 O.A. Reutov, K.P. Butin and I.P. Beletskaya, Usp. Khim., 43 (1974) 35.
22 K.P. Butin, I.P. Beletskaya and O.A. Reutov, J. Organometal, Chem., 64 (1973) 323.
23 D.P.N. Stachell and R.S. Satchell, Usp. Khim., 42 (1973) 1009.
24 R.P. Bell and E. Gelles, Proc. Roy. Soc. (London), A 210 (1952) 310.
25 M.N. Vargaftik and Ya.K. Sirkin, Izv. Akad. Nauk. SSSR, Ser. Khim., (1974) 263.
26 F. Basolo and R. Pearson, Mekhanismi neorganicheskikh reactsii, Mir, Moscow, 1971.

27 K.P. Butin, A.N. Kashin, I.P. Beletskaya and D.A. Reutov, J. Organometal. Chem., 16 (1968) 27.

28 G. Costa, Zh. Vses. Khim. Obshch., im D.I. Mendeleeva, 17 (1972) 420.

29 R.M. Salinger and R.E. Dessy, Tetrahedron Lett., 11 (1963) 729.

30 R.G. Pearson (Ed.), Hard and soft acids and bases, Dowden, Hutchison and Ross Inc., Stroudsburg, Penn., 1973.

31 F. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Vol. 2, Mir, Moscow, 1969.

32 B.V. Nekrasov, Osnovi obshchii khimii, Vol. 2, Khimia, Moscow, 1973.

33 C.D. Ritchie, Interaction in Dipolar Aprotic Solvents, in Solute—Solvent Interaction, Marcel Dekker, New York, 1969.

34 B.W. Clare, D. Cook, E.C.F. Ko, Y.C. Mac and A.J. Parker, J. Amer. Chem. Soc., 88 (1966) 1911.

35 K.P. Butin, A.N. Kashin, I.P. Beletskaya, L.S. German and V.R. Polishchuk, J. Organometal. Chem., 25 (1970) 11.

36 I.N. Rozhkov and I.L. Knunynts, Dokl. Akad. Nauk SSSR, 199 (1971) 614.

37 D. Cram, Fundamentals of Carbanion Chemistry, Mir, Moscow, 1967.

38 N.G. Faleev, Yu.N. Belokon and V.M. Belikov, Izv. Akad. Nauk SSSR, Ser. Khim., (1970) 73.

39 K.P. Butin, Thesis, Moscow State University, Moscow, 1974.

40 J.C. Baldwin, M.F. Lappert, J.B. Pedley and J.S. Poland, J. Chem. Soc. Dalton Trans., (1972) 1943.

41 M.T. Beck, Chimia ravnovesii reaktsii komplexoobrazovaniya, Mir, Moscow, 1973.

42 C.K. Jorgensen, Inorg. Chem., 3 (1964) 1201.

43 R.G. Pearson, Inorg. Chem., 12 (1973) 712.

44 R.G. Pearson and I. Zongstag, Usp. Khim., 38 (1969) 1223.

45 C.S. Ferbes and H.H. Anderson, J. Amer. Chem. Soc., 66 (1944) 931.

46 G. Calingaert, H.A. Beatty and N.R. Neal, J. Amer. Chem. Soc., 61 (1939) 2748, 2755.

47 K. Kuhlein and W.P. Neuman, Justus Liebigs Ann. Chem., 702 (1967) 17.

48 J.G.A. Luijten and F. Rijkens, Rec. Trav. Chim. Pays-Bas, 83 (1964) 857.

49 G.J.M. van der Kerk, F. Rijkens and M.J. Janssen, Rec. Trav. Chim. Pays-Bas, 81 (1962) 764.

50 F. Rijkens and G.J.M. van der Kerk, Rec. Trav. Chim. Pays-Bas, 83 (1964) 723.

51 E.J. Bulten and W. Drenth, J. Organometal. Chem., 61 (1973) 179.

52 O.P. Sutkina, E.M. Popov and K.A. Kocheshkov, Zh. Obshch. Khim., 41 (1971) 1271.

53 H. Muller and J.R. Van Wazer, J. Organometal. Chem., 23 (1970) 395.

54 S.C. Pace, J.-C. Elkaim and J.G. Riess, J. Organometal. Chem., 56 (1973) 141.

55 M.G. Voronkov, I.A. Keiko and T.A. Kuznetsova, Zh. Obshch. Khim., 43 (1973) 1862.

56 D.R. Weyenberg, A.E. Bey, H.F. Stewart and W.H. Atwell, J. Organometal. Chem., 6 (1966) 583.

57 L.G. Mahone and D.R. Weyenberg, J. Organometal. Chem., 12 (1968) 231.

58 K. Moedritzer and J.R. Van Wazer, Inorg. Chem., 6 (1967) 93.

59 K. Moedritzer and J.R. Van Wazer, J. Inorg. Nucl. Chem., 28 (1966) 957.

60 K. Moedritzer and J.R. Van Wazer, J. Organometal. Chem., 6 (1966) 242.

61 H.H. Anderson, J. Amer. Chem. Soc., 73 (1951) 5801.

62 K. Moedritzer and J.R. Van Wazer, Inorg. Chem., 7 (1968) 2105.

63 J.R. Van Wazer, K. Moedritzer and L.C.D. Groenweghe, J. Organometal. Chem., 5 (1966) 420.

64 D.A. Armitage and A. Tarassolli, Inorg. Nucl. Chem. Lett., 9 (1973) 1225.

65 K. Moedritzer and J.R. Van Wazer, J. Organometal. Chem., 12 (1968) 69.

66 D.R. Weyenberg, A.E. Bey and P.I. Ellison, J. Organometal. Chem., 3 (1965) 489.

67 P.D. Zemany and F.P. Price, J. Amer. Chem. Soc., 70 (1948) 4222.

68 R.O. Sauer and E.M. Hatsell, J. Amer. Chem. Soc., 70 (1948) 3590.

69 G.A. Russell, J. Amer. Chem. Soc., 81 (1959) 4815.

70 E.A.V. Ebsworth, A.G. Lee and G.M. Sheldrick, J. Chem. Soc. A, (1968) 2294.

71 A. Stock and C. Somieski, Ber. Deut. Chem. Ges., 52 (1919) 719.

72 K.N. Kobrakov, T.I. Chernisheva, L.I. Kartashova and N.S. Nametkin, Dokl. Akad. Nauk SSSR, 202 (1972) 343.

73 J.W. Ryan, J. Amer. Chem. Soc., 84 (1962) 4730.

74 H.H. Anderson, J. Amer. Chem. Soc., 66 (1944) 935.

75 H. Weingarten and J.R. Van Wazer, J. Amer. Chem. Soc., 88 (1966) 2500.

76 J.R. Van Wazer and K. Moedritzer, J. Inorg. Nucl. Chem., 26 (1964) 737.

77 K. Moedritzer and J.R. Van Wazer, Inorg. Chem., 5 (1966) 1254.

78 K. Moedritzer and J.R. Van Wazer, Inorg. Chem., 5 (1966) 574.

79 L.E. Nelson, N.C. Angelotti and D.R. Weyenberg, J. Amer. Chem. Soc., 85 (1963) 2662.

80 B. Suryanarayanan, B.W. Peace and K.G. Mayhan, J. Organometal. Chem., 55 (1973) 65.

81 B.N. Dolgov, S.N. Borisov and M.G. Voronkov, Zh. Obshch. Khim., 27 (1957) 2062.

82 C.G. Pitt and K.R. Skillern, J. Organometal. Chem., 7 (1967) 525.

83 P. Jutzi and H.J. Hoffmann, J. Organometal. Chem., 40 (1972) C 61.

84 K.R. Beck and R.A. Benkeser, J. Organometal. Chem., 21 (1970) P35.

85 K. Moedritzer and J.R. Van Wazer, J. Organometal. Chem., 13 (1968) 125.

86 K. Moedritzer and J.R. Van Wazer, J. Amer. Chem. Soc., 87 (1965) 2360.
87 G.M. Burch and J.R. Van Wazer, J. Chem. Soc. A, (1966) 586.
88 K. Moedritzer, J.R. Van Wazer and R.E. Miller, Inorg. Chem., 7 (1968) 1636.
89 F.H. Pollard, G. Nicklesse and D.C. Uden, J. Chromatogr., 19 (1965) 28.
90 A.K. Sawyer, J.E. Braun and E.L. Hanson, J. Organometal. Chem., 3 (1965) 464.
91 W.P. Neuman and J. Pedain, Tetrahedron Lett., (1964) 2461.
92 A.G. Davies and P.G. Harrison, J. Chem. Soc. C, (1967) 298.
93 H.G. Kuivila, R. Sommer and D.C. Green, J. Org. Chem., 33 (1968) 1119.
94 L.S. Melnichenko, N.N. Zemlyansky, N.D. Kolosova, I.V. Karandi and K.A. Kocheshkov, Dokl. Akad. Nauk SSSR, 198 (1971) 1094.
95 N.N. Zemlyansky, I.P. Goldshtein, E.N. Guryanova, O.P. Sutkina, E.M. Panov, N.A. Slovokhotova and K.A. Kocheshkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1967) 728.
96 I.P. Goldshtein, E.B. Guryanova, N.N. Zemlyansky, O.P. Sutkina, E.M. Panov and K.A. Kocheshkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1967) 2201.
97 W.P. Neuman and G. Burkhart, Justus Liebigs Ann. Chem., 663 (1963) 13.
98 E.V. van den Berghe and G.P. van der Kelen, J. Organometal. Chem., 6 (1966) 522.
99 D. Grant and J.R. Van Wazer, J. Organometal. Chem., 4 (1965) 229.
100 W.P. Neumann and R. Sommer, Angew. Chem., 75 (1963) 788.
101 M.B. Bochkarev, S.P. Korneva, L.P. Mayorova, V.A. Kusnetsov and N.S. Vyazankin, Zh. Obshch. Khim., 44 (1974) 308.
102 H.M.J.C. Creemers, F. Verbeek and J.G. Noltes, J. Organometal. Chem., 8 (1967) 469.
103 L.C. Willemsens and G.J.M. van der Kerk, J. Organometal. Chem., 13 (1968) 357.
104 P.R. Austin, J. Amer. Chem. Soc., 54 (1932) 3287.
105 V.F. Mironov and D.L. Kravchenko, Dokl. Akad. Nauk SSSR, 158 (1964) 656.
106 S. Cradock and E.A.V. Ebsworth, J. Chem. Soc. A, (1967) 1226.
107 W. Wolfsberger and H.H. Pickel, J. Organometal. Chem., 54 (1973) C8.
108 P.G. Harrison and J.J. Zuckerman, Inorg. Chem., 9 (1970) 175.
109 K.A. Kocheshkov, A.A. Mokhina, N.N. Zemlyansky and E.M. Panov, Izv. Akad. Nauk SSSR, Ser. Khim., (1969) 1381.
110 K.A. Kocheshkov, N.V. Fomina, N.N. Sheverdina, N.N. Zemlyansky and V.A. Chernoplekova, Izv. Akad. Nauk SSSR, Ser. Chim., (1973) 711.
111 I.F. Lutsenko, Yu.I. Baukov and G.S. Burlachenko, J. Organometal. Chem., 6 (1966) 496.
112 A. Singh, A.K. Rai and R.C. Mehrotra, J. Organometal. Chem., 57 (1973) 301.
113 H.H. Anderson, J. Amer. Chem. Soc., 72 (1950) 2091.
114 H.J. Emeleus and A.G. Maddock, J. Chem. Soc., (1944) 293.
115 L.S. Melnichenko, N.N. Zemlyansky and K.A. Kocheshkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 2055.
116 O.P. Sutkina, E.M. Panov and K.A. Kocheshkov, Zh. Obshch. Khim., 43 (1973) 1922.
117 L.S. Melnichenko, N.N. Zemlyansky, K.A. Samyrskaya and K.A. Kocheshkov, Dokl. Akad. Nauk SSSR, 190 (1970) 351.