103. *Co-ordination Compounds having Carboxylic Esters as Ligands. Part II.*[1] *Relative Acceptor Strengths of Some Group III and IV Halides.**

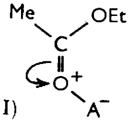
By M. F. Lappert.

The infrared spectroscopic shifts in carbonyl stretching frequencies as between free ethyl acetate and its complexes with various Group III and IV halides have been recorded and interpreted in terms of relative acceptor strengths of the halides, within related series and with respect to ethyl acetate (which has very low steric requirements) as the reference base. This provides the order Br > Cl for B and Al, but Cl > Br for In and the Group IV halides, and Group trends are B > Ga > Al > In, Sn > Ge > Si, and Ti > Zr. Comparisons are made with data from other sources.

The infrared spectrum of $ZrCl_4,2EtOAc$ indicates that the compound has a *cis*-octahedral configuration, whereas the other 1 : 2 complexes probably have a *trans*-configuration.

One drawback in the Lewis theory of acids and bases is its failure satisfactorily to come to terms with quantitative aspects. This may be illustrated by the fact that only limited attention has so far been paid to the general problem of the relative acceptor strengths of Lewis acids with regard to particular reference bases, although the converse problem of the relative donor strengths of bases has been studied more deeply, especially from the standpoints of the steric requirements of the base (for a summarising article, see ref. 2) and of classification of acceptor atoms.[3] The reasons are, at least in part, due to the laborious methods at present required for quantitative measurements.[4] These involve the calculation or measurement of the enthalpy change accompanying the formation (most meaningfully, in the gas phase) of the complex from its donor and acceptor components, either by calorimetry or from equilibrium studies, or from the dipole moment of the donor–acceptor bond. More qualitative assessments have been made by differential calorimetry,[5] by comparative tabulations of the range of complexes formed by particular acceptors, by displacement [*i.e.*, using the argument that a stronger base (acid) generally displaces a weaker base (acid) from a complex] or competition reactions, or by measurement of relative catalytic effects of Lewis acids, for example in Friedel–Crafts reaction or cationic polymerisation.

We have tried to provide a simpler and more rapid method of investigating relative acceptor properties of closely related series of Lewis acids. In principle, we use a highly polarisable reference donor and measure the changes in polarisation that follow complex formation. Ethyl acetate was chosen as the donor because of the absence of complicating competition reactions (*e.g.*, aldehydes also undergo carbonyl addition with boron trichloride,[6] whilst acyl chlorides often afford, not only complexes with oxygen as donor, but also with chlorine,[7] such as $[CH_3{\cdot}CO]^+[AlCl_4]^-$) and because of its small steric requirements (see below). It has been shown in Part I that the donor site is provided by the acyl-oxygen atom (cf. I) and not the alkyl-oxygen atom. Accordingly, complex formation requires perturbation of the C=O bond and the strength of the donor–acceptor bond must be reflected in the extent of polarisation of the C=O bond. This, in turn, may be measured by the change in the C=O bond stretching force constant or, as a first



(I)

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* For preliminary results see International Conference on Co-ordination Chemistry, London, 1959 (*Chem. Soc. Spec. Publ.*, No. 13, p. 179).

[1] Part I, Lappert, *J.*, 1961, 817.

[2] Brown, *J.*, 1956, 1248.

[3] Ahrland, Chatt, and Davies, *Quart. Rev.*, 1958, **12**, 265.

[4] Cf. Stone, *Chem. Rev.*, 1958, **58**, 101.

[5] Lindqvist and Zackrisson, *Acta Chem. Scand.*, 1960, **14**, 453.

[6] Frazer, Gerrard, and Lappert, *J.*, 1957, 739.

[7] Susz and Wuhrmann, *Helv. Chim. Acta*, 1957, **40**, 722; Cook, *Canad. J. Chem.*, 1959, **37**, 48.

approximation, by the change in the C=O bond stretching frequency. References in support of this proposition were cited in Part I.

The validity of our method is also to be judged by its results and by comparison with those of other methods. At this time comparisons are only approximate since our results relate to ethyl acetate, whereas data from other sources are for different donors (particularly tertiary amines) as reference bases. However, even with this severe limitation, qualitative agreement appears to be good. Further, our results appear to offer chemically acceptable correlations. Differences from other data may sometimes reasonably be attributed to the exceedingly low steric requirements of ethyl acetate as a base. In the first instance, this is due to the acyl-oxygen atom's being only two-co-ordinate in an ester complex. This is an unusually low co-ordination number for a donor atom (*e.g.*, the nitrogen atom in an amine complex is four-co-ordinate). Secondly, even at the β-atom in an ester complex (*i.e.*, the acyl-carbon), the bond angles (~120°) are such that the groups pendant from the acyl-carbon are held well back from the acceptor portion (see also Part I).

Boron Trihalides.—The shifts ($\Delta\nu$) in carbonyl stretching frequencies between the free ester and the complexes are shown in Table 1. Also included, for rough comparison, are literature data obtained by other methods on the boron trihalide–pyridine or trimethylamine systems. The $\Delta\mu(N^+–B^-)$ values are by Bax, Katritzky, and Sutton,[8] and were regarded as donor–acceptor relative bond dipole moments with respect to specific reference bases. They were calculated [$\Delta\mu(N^+–B^-) = \mu - \mu(CHX_3)$] from the measured dipole moment of the amine–boron halide complex (μ) and that of the appropriate halogenoform [$\mu(CHX_3)$]; the latter term was introduced, since it is as nearly as possible equivalent to the $-BX_3$ dipole contribution in the complex. The $-\Delta H_f$ values, other than those shown in parenthesis, are due to Brown and Holmes [9] and represent the enthalpy change for: BX_3 (l) + py (in $PhNO_2$ soln.) = py,BX_3 (in $PhNO_2$ soln.); those in parentheses, due to Greenwood and Perkins,[10] are for the enthalpy change accompanying the gas-phase formation of the complex and were computed by using estimated approximations for the heats of sublimations of the pyridine–boron trihalide complexes.

TABLE 1.

Boron trihalides.

X in base, BX_3	$\Delta\nu$ (cm.$^{-1}$)	$\Delta\mu(N^+–B^-)$ (D)[8] Reference base		$-\Delta H_f$ (kcal. mole^{-1}) [9, 10]
		Me_3N	py	
F	119	4·04	5·31	31·7
Cl	176	5·13	6·52	39·5 (37·9)
Br	191	5·57	6·90	44·5 (43·5)

The three methods give qualitative ($BBr_3 > BCl_3 > BF_3$) and semiquantitative agreement. Even if the comparative data were all with ethyl acetate as the reference donor, it is doubtful whether very close quantitative agreement, except as between the spectroscopic and the dipole-moment methods, should be expected. To analyse this proposition, it is necessary to consider the factors (see refs. 4, 8, 9, and 10) which are likely to be significant in controlling the acceptor power of the boron atom in its different environments. On the one hand, p_π–p_π B–X bonding (mesomeric effect) and X/Base repulsion phenomena are in agreement with the observed order; on the other, the electronegativity of the halogen (inductive effect) and halogen size act in the reverse order. The heat of formation of an addition compound in the gas phase incorporates, not only the heat of formation of the donor-acceptor bond, but also the energy of reorganisation of the donor and acceptor parts.[11] Especially important is the latter term which is primarily concerned

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[8] Bax, Katritzky, and Sutton, *J.*, 1958, 1258.

[9] Brown and Holmes, *J. Amer. Chem. Soc.*, 1956, **78**, 2173.

[10] Greenwood and Perkins, *J.*, 1960, 1141.

[11] Bauer, Finlay, and Laubengayer, *J. Amer. Chem. Soc.*, 1943, **65**, 889.

with the energy difference due to change of hybridisation of the boron orbitals from sp^2 to sp^3,[12] and this factor is not likely to be of the same importance in the spectroscopic and the dipole-moment method.

Comparisons between Trichlorides and Tribromides of Aluminium and Indium.—The results are shown in Table 2. The inferences are that, with ethyl acetate as reference base, the relative acceptor strengths for the aluminium trihalides are Br $>$ Cl and for the indium trihalides Cl $>$ Br. This is chemically reasonable, for Greenwood and Perkins[13] computed heats of formation for gallium chloride– and bromide–pyridine complexes in the gas-phase as $-35{\cdot}2$ and $-38{\cdot}3$ kcal. mole^{-1}, respectively. Since in the boron trihalide series the acceptor order is also Br $>$ Cl, it is acceptable that it should be so for the aluminium halides. Further, the heats of reaction[13] of aluminium trichloride and tribromide with acetophenone, benzophenone, acetaldehyde, and nitrobenzene are in the order Br $>$ Cl. The order Br $>$ Cl for the acceptor strengths of Group III trihalides is largely to be interpreted in terms of the greater capacity for M–Cl than for M–Br p_π–p_π bonding. However, this effect is likely to become progressively less important (see also ref. 9) as M increases in atomic number, since π-bonding becomes much less significant when high-energy p-orbitals are involved (thus, of course, π-bonding increases in the order Br $<$ Cl $<$ F). That the enthalpy difference between the chloride and bromide complexes of boron is greater than that of gallium is consistent also with this interpretation.

TABLE 2.

Carbonyl shifts for $EtOAc,MX_3$.

Complex	$EtOAc,AlCl_3$	$EtOAc,AlBr_3$	$EtOAc,InCl_3$	$EtOAc,InBr_3$
$\Delta\nu$ (cm.$^{-1}$)	117	138	113	107

Relative Acceptor Strengths of the Group III Chlorides and Bromides.—The carbonyl shift for the gallium trichloride–ethyl acetate complex (141 cm.$^{-1}$) has also been recorded. With ethyl acetate as the reference base, the relative acceptor strengths for the trichlorides are B $>$ Ga $>$ Al $>$ In and for the tribromides are B $>$ Al $>$ In (results on $EtOAc,GaBr_3$ are not available). This appears to be reasonable since it reflects (B $>$ Ga $>$ Al) the increasing ability of the metal to accept electronic charge from the base with increasing Pauling electronegativity order (B, 2·0; Ga, 1·6; Al, 1·5). It also recalls the relative acid strengths (ionic dissociation in water) of the hydroxides: $B(OH)_3 > Ga(OH)_3 > Al(OH)_3$. This comparison is relevant since there is evidence[14] that the ionic dissociation of boric acid in water is represented by $B(OH)_3 + H_2O \rightleftharpoons [B(OH)_4]^-H^+$ rather than by $B(OH)_3 \rightleftharpoons [(HO)_2BO]^-H^+$. The seemingly curious position in this series of gallium *vis à vis* aluminium is undoubtedly also connected with Al^{3+} having the inert-gas configuration of electrons, whereas Ga^{3+} has in addition a complete outer d-shell.

With pyridine as the reference base, the thermochemical results mentioned above support the order B $>$ Ga for chlorides and bromides (comparative calculations[13] on aluminium halides fit less well, but they are based on rather early thermochemical measurements, the accuracy of which is perhaps questionable).

Relative acceptor strengths of the Group III alkyls are summarised in Table 3 for comparison. The conclusion[15] from the thermochemical data is that, with trimethylamine as reference base, the acceptor strengths of the Group III trimethyls (methyl and chlorine groups have very similar steric requirements[16]) are in the order Al $>$ Ga $>$ In $>$ B, and the same order[17] holds for the triethyl compounds with dioxan as the base.

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[12] Cotton and Leto, *J. Chem. Phys.*, 1959, **30**, 993.

[13] Greenwood and Perkins, *J.*, 1960, 1145.

[14] Torssell, *Arkiv Kemi*, 1957, **10**, 541.

[15] Coates and Whitcombe, *J.*, 1956, 3351.

[16] Brown, Barbaras, Berneis, Bonner, Johannessen, Grayson, and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 1.

[17] Strohmeier and Hümpfner, *Z. Elektrochem.*, 1957, **61**, 1010.

This sequence differs from that referred to earlier, the positions of boron being especially irreconcilable. This may be attributed, at least in part, to steric factors.[4] The *F*-strain in MeN,MMe$_3$ will be greatest when M has the smallest covalent radius, and indeed Brown and Johannesen[18] have estimated that in the absence of steric effects the heat of formation of trimethylamine–trimethylborane would be 25·4 kcal. mole^{-1}.

TABLE 3.

Group III trialkyls.

M in base,MR$_3$	B	Al	Ga	In
$-\Delta H_f$ (kcal. mole^{-1}) *	17·6 [a]	‡	21·0 [b]	19·9
μ(D) †	0·3	3·5	2·1	0·8$_7$

* Results for gas-phase dissociation of Me$_3$N,MMe$_3$. † Results for MEt$_3$ in dioxan (Strohmeier and Hümpfner, *Z. Elektrochem.*, 1957, **61**, 1010). ‡ Too stable to permit study (Davidson and Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 316; Coates and Huck, *J.*, 1952, 4511).

[a] Brown, Taylor, and Gerstein, *J. Amer. Chem. Soc.*, 1944, **66**, 431; Brown and Gerstein, *ibid.*, 1950, **72**, 2923. [b] Coates, *J.*, 1951, 2003; Coates and Hayter, *J.*, 1953, 2519. [c] Coates and Whitcombe, *J.*, 1956, 3351.

Dipole-moment measurements on Group III trichlorides in dioxan (B, 4·9;[19] Al, 2·0; Ga, 5·1;[20] In, 4·0) indicate, for that base, the order Ga > B > In > Al. These results must be interpreted with considerable caution since the stoicheiometry of the Group III trihalide complexes with dioxan is variable. Thus, boron trichloride not only forms a 1 : 1 complex with dioxan,[21] but also a complex (BCl$_3$)$_3$,2C$_4$H$_8$O$_2$.[22] Aluminium and gallium trichloride probably form 1 : 1 complexes, but indium trichloride forms both a 1 : 1 and a 1 : 2 complex with dioxan.[23] Indeed complexes of type MX$_3$,2R$_2$O appear more frequently than the 1 : 1 types for indium.

Information on the relative reactivities of some Group III trihalides is also available. For example, in Friedel–Crafts benzoylation [24,25] and acetylation [24] the catalyst activity order is BCl$_3$ < AlCl$_3$ < GaCl$_3$, whilst for cationic polymerisation of isobutene the order is AlBr$_3$ > BBr$_3$.[26] Such results are difficult to interpret in terms of relative acceptor strengths because of possible variations in kinetics, mechanism, and catalyst specificity, and because of co-catalysis (particular in polymerisation [27]) with the different halides. However, the order Ga > Al > B for the chlorides is fairly certain when the reference base is the chloride ion, *i.e.*, the complex is [MCl$_4$]$^-$ (see, *e.g.*, acetyl chloride–BCl$_3$ and –GaCl$_3$ systems [24]). The anomalous position of boron in this series may be due to a steric effect, although the existence of the [BCl$_4$]$^-$ ion is established.[28]

TABLE 4.

Carbonyl shifts for titanium(IV) and zirconium(IV) halide complexes.

Complex	TiCl$_4$,EtOAc	TiBr$_4$,EtOAc	TiBr$_4$,2EtOAc	TiI$_4$,2EtOAc	ZrCl$_4$,2EtOAc
$\Delta\nu$ (cm.$^{-1}$)	128	128	128 *	112 †	104/128

* Shoulder at $\Delta\nu$ = 102 cm.$^{-1}$. † Shoulder at $\Delta\nu$ = 80 cm.$^{-1}$.

Titanium(IV) *and Zirconium*(IV) *Halides*.—Available results are shown in Table 4. The spectrum of the zirconium tetrachloride complex, taken on a liquid specimen, showed a carbonyl doublet, the two bands being of almost identical intensity. This strongly

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[18] Brown and Johannesen, *J. Amer. Chem. Soc.*, 1953, **75**, 16.

[19] Lane, McCusker, and Curran, *J. Amer. Chem. Soc.*, 1942, **64**, 2076.

[20] Miltenberger, Dissertation, Würzburg, 1957; quoted by Strohmeier and Nützel, *Z. Elektrochem.*, 1958, **62**, 188.

[21] Holliday and Sowler, *J.*, 1952, 11.

[22] Frazer, Gerrard, and Mistry, *Chem. and Ind.*, 1958, 1263.

[23] Fairbrother, Flitcroft, and Prophet, *J. Less-Common Metals*, 1960, **2**, 49.

[24] Greenwood and Wade, *J.*, 1956, 1527.

[25] Jensen and Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 3039.

[26] Fairbrother and Seymour, unpublished work; Seymour, Ph.D. Thesis, Manchester, 1943.

[27] Pepper, *Quart. Rev.*, 1954, **8**, 88.

[28] Lappert, *Proc. Chem. Soc.*, 1957, 121.

points to a *cis*-octahedral form for the complex: coupling between the two C=O vibrations through the metal (Zr) atom would give rise to symmetric and antisymmetric modes, which would both be infrared active. A *cis*-configuration was also indicated from dipole-moment measurements.[29]

The failure to observe similar carbonyl doublets in the spectra of the two 1 : 2 titanium bromide and iodide complexes, despite the use of calcium fluoride optics, suggests that these are of *trans*-octahedral symmetry. In a *trans*-complex the coupled symmetric C–O stretching mode would be infrared-inactive, since such a vibration does not produce a net dipole-moment change.

The relative acceptor strengths of the various halides with respect to ethyl acetate appear to be $TiCl_4 \approx TiBr_4 > TiI_4$ and titanium and zirconium tetrachloride seem to be about equal, the former probably slightly the stronger. Caution is needed as the comparisons are of compounds that may have different stereochemistry, but this difficulty may not be serious since the shifts obtained with titanium(IV) bromide are not even sensitive to stoicheiometry. Comparisons may be made with the work of Emeléus and Rao [30] on dissociation pressures of titanium(IV) and zirconium(IV) halides with various ligands and on the enthalpies of formation of the 1 : 2 titanium(IV) halide–pyridine complexes in the gas phase (which are $33\text{-}L_F$, $39\text{-}L_{Cl}$, $31\text{-}L_{Br}$, and $23\text{-}L_I$ kcal. mole^{-1} for the fluoride to iodide complexes, respectively; the L_X terms represent the unknown latent heats of sublimation of the complexes, which, however, were assumed to be approximately the same for each complex). This generally shows the order $Cl > Br > I > F$ and $Ti^{IV} > Zr^{IV}$ in terms of relative acceptor strengths.

Silicon(IV), *Germanium*(IV), *and Tin*(IV) *Chlorides*.—There was no heat of mixing of ethyl acetate with silicon(IV) or germanium(IV) chloride and the infrared spectrum of each solution between 5000 and 650 cm.$^{-1}$ was that of pure ethyl acetate, with only a very slight shift of the carbonyl stretching frequency ($\Delta\nu$: $SiCl_4$, 4; $GeCl_4$, 4 cm.$^{-1}$). The spectrum of each solution (1 : 1 and 1 : 2 EtOAc, molar) was next examined in a variable temperature cell, because it was thought possible that a complex might be stabilised in the solid state by its lattice energy. With liquid nitrogen as the cell-coolant, evidence of weak interaction was obtained (see Figure for $SiCl_4$,2EtOAc; the $GeCl_4$,2EtOAc spectra were similar and are therefore not reproduced) for the solid solutions. For the silicon tetrachloride system, the principal carbonyl peak (now at 1727 cm.$^{-1}$) showed well-defined shoulders at 1685 and 1655 cm.$^{-1}$; and the germanium tetrachloride system had a main peak at 1725 cm.$^{-1}$ and shoulders at 1680 and 1647 cm.$^{-1}$. Tin(IV) chloride, on the other hand, formed a stable 1 : 2 EtOAc complex, which showed a single (even in the liquid phase), sharp carbonyl stretching absorption at 1613 cm.$^{-1}$ (*i.e.*, $\Delta\nu$ 128 cm.$^{-1}$); the absence of a carbonyl doublet indicates that the complex is *trans*-octahedral. Thus with ethyl acetate as base, there is little to choose between silicon and germanium tetrachloride (with possibly $Ge > Si$) but both are much weaker acceptors than tin.

The order $Sn^{IV} \gg Ge^{IV} > Si^{IV}$ is corroborated for dioxan as reference base, by dipole-moment studies [19] (μ in dioxan: $SiCl_4$, 0·0; $GeCl_4$, 0·7; $SnCl_4$, 3·8 D). Moreover, although all three chlorides form stable complexes with some nitrogen donors, *e.g.*, pyridine,[31] complexes with oxygen donors for silicon(IV) and germanium(IV) chloride are rare, although they are common and stable with tin(IV).

Tin(IV) *Halides*.—Tin(IV) bromide was investigated for comparison with the chloride and particularly to ascertain whether the order of acceptor strengths (generally, $Br > Cl$) persisted also when the central metal had available only *d*-, and not *p*-, orbitals for π-bonding (with halogen) or σ-bonding (with donor). Qualitative information [32] about the

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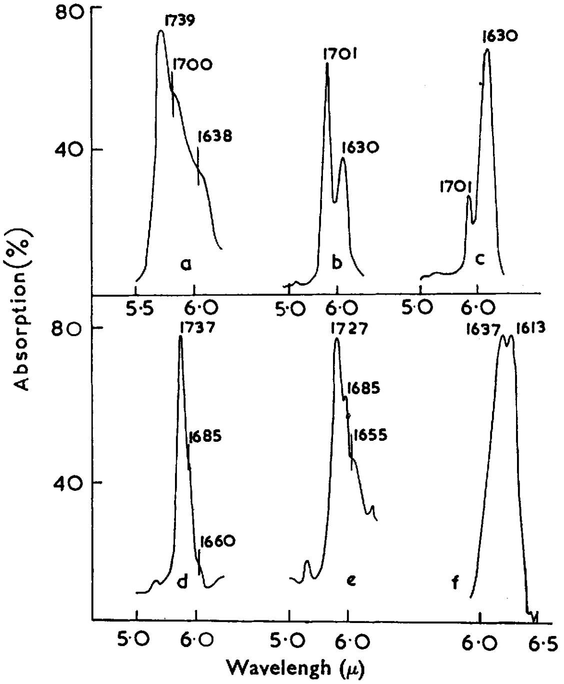
[29] Osipov and Kletenik, *Zhur. obshchei Khim.*, 1957, **27**, 2921.

[30] Emeléus and Rao, *J.*, 1958, 4245.

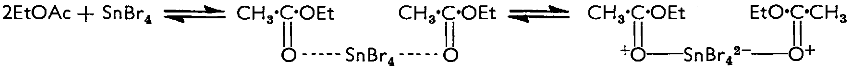
[31] (Si) Harden, *J.*, 1887, **51**, 40; (Ge) Abel, *J.*, 1958, 3746; (Sn) Pfeiffer, *Z. anorg. Chem.*, 1911, **71**, 97.

[32] *E.g.*, Pfeiffer and Halperin, *Z. anorg. Chem.*, 1914, **87**, 335.

number of different types of ligands that form complexes with the tin(IV) halides indicates the reverse order (normally, Cl > Br > I) and our work confirms this, and not only from the $\Delta\nu$ values ($SnCl_4$, 128; $SnBr_4$, 111 cm.$^{-1}$). The spectrum of the tin(IV) bromide complex shows a predominant single peak for the carbonyl stretching frequency only in the solid state; in the liquid there is a doublet (1701 and 1630 cm.$^{-1}$) (see Figure). The complex was soluble in n-pentane, and the spectrum showed a main peak at 1739 cm.$^{-1}$ and well-defined shoulders at 1700 and 1638 cm.$^{-1}$. These observations suggest a state of equilibrium involving (II), (III), and (IV), with (IV) predominant only in the solid phase where there is lattice energy stabilisation of the weak complex. The equilibrium state (III), characterised by ν(C=O) 1700 cm.$^{-1}$, probably represents a bonding situation akin to hydrogen bonding. The spectra of $SiCl_4$,2EtOAc and $GeCl_4$,2EtOAc show also (see Figure for $SiCl_4$,2EtOAc) the existence of the equilibrium (II) $\rightleftharpoons$ (III) $\rightleftharpoons$ (IV), with the situation (II) predominant even in the solid phase.



Infrared spectra (carbonyl region, maxima in cm.$^{-1}$) of (a) $SnBr_4$,2EtOAc in n-pentane, (b) $SnBr_4$,2EtOAc (liquid, 20°), (c) $SnBr_4$,2EtOAc (solid, cold-cell with liquid nitrogen as coolant), (d) $SiCl_4$,2EtOAc (liquid, 20°), (e) $SiCl_4$,2EtOAc (solid, cold-cell with liquid nitrogen as coolant), and (f) $ZrCl_4$,2EtOAc (liquid).



$$2\text{EtOAc} + \text{SnBr}_4 \rightleftharpoons \begin{array}{c}\text{CH}_3\cdot\text{C}\cdot\text{OEt}\\ \| \\ \text{O}\end{array}\text{-----}\,\text{SnBr}_4\,\text{-----}\begin{array}{c}\text{CH}_3\cdot\text{C}\cdot\text{OEt}\\ \| \\ \text{O}\end{array} \rightleftharpoons \begin{array}{c}\text{CH}_3\cdot\text{C}\cdot\text{OEt}\\ \| \\ {}^{+}\text{O}\end{array}\text{——SnBr}_4{}^{2-}\text{——}\begin{array}{c}\text{EtO}\cdot\text{C}\cdot\text{CH}_3\\ \| \\ \text{O}^{+}\end{array}$$

(II) (III) (IV)

Experimental.—Most of the complexes were those prepared as described in Part I. New ones are $InBr_3$,EtOAc (white, low-melting, crystalline); $TiBr_4$,EtOAc (rust-purple, crystalline); $TiBr_4$,2EtOAc (orange-purple, pasty solid), and TiI_4,2EtOAc (black, pasty solid). The colourless, viscous complex $ZrCl_4$,2EtOAc was also prepared.[33]

Infrared spectra of these additional compounds were taken on a Perkin-Elmer model 21

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[33] Rosenheim and Hertzmann, *Ber.*, 1907, **40**, 810.

spectrophotometer with calcium fluoride optics. The spectra of the other compounds were taken on a Grubb-Parsons S3A double-beam spectrophotometer, with rock-salt optics, as described in Part I. Calibrations, based on water vapour, were carried out for each run. Some of the measurements on the complexes with silicon and germanium tetrachloride and with tin tetrabromide were carried out with a low-temperature cell and a variable path-length; these are included in the Figure.

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