Journal of Organometallic Chemistry, 136 (1977) 315—322

LEWIS ACIDITY OF ORGANOSILICON ACETATES

D.P. GRADDON and B.A. RANA
School of Chemistry, University of New South Wales, Kensington, N.S.W. 2033 (Australia)
(Received March 23rd, 1977)

Summary

Thermodynamic data, obtained calorimetrically, are reported for the formation of adducts of organosilicon acetates, $R_nSi(OCOMe)_{4-n}$ ($0 \leqslant n \leqslant 3$) with a wide variety of Lewis bases in acetonitrile solution. Only 1/1 adducts are formed, in which the silicon is 5-coordinate and there is evidence that the coordination number cannot exceed five in these compounds. Enthalpies of adduct formation ($-\Delta H^0$) increase regularly as R is replaced by OCOMe and become very large with $Si(OCOMe)_4$, exceeding 150 kJ mol^{-1} for addition of amines to this compound. Despite the large enthalpies of formation, adduct stabilities are not high and adduct formation constants, K, rarely exceed 200 l mol^{-1}; stabilites are similar for $0 \leqslant n \leqslant 2$ but a little greater for $n = 3$ and are thus little affected by variations in the enthalpy.

Introduction

Silicon, like carbon, usually has a covalency of four, but it also resembles the heavier Group IV elements in forming compounds with the coordination number expanded to five or six. While the complex fluoride ion, SiF_6^{2-}, is probably the most familiar example of this, complex organosilicon fluorides of the types $RSiF_4^-$ and $R_2SiF_3^-$ have been isolated [1] and various adducts of silicon halides with bases, such as pyridine, have long been known, though their structures remain uncertain [2]. Lewis acidity is less common when the silicon is bound to oxygen but can be observed in the chelate, 6-coordinate acetylacetone complex ion, $Si(acac)_3^+$; in $Me_2Si(acac)_2$ on the other hand the acetylacetone ligands appear to be unidentate and the silicon 4-coordinate [3]. Recently chelate, 6-coordinate complex oxalates, $Si(C_2O_4)_3^{2-}$, have been prepared [4], the complex acetate $K_2[Si(OCOMe)_6]$ isolated and the presence of the 5-coordinate ion, $Si(OCOMe)_5^-$ demonstrated in solution [5]. A series of organosilicon cage derivatives of triethanolamine has been shown by X-ray analysis to be 5-coordinate [6], as has a similar compound derived from diethanolamine [7].

In spite of these examples and the general acceptance that some 5-coordinate intermediates are involved in substitution reactions at silicon centers, the Lewis acidity of silicon compounds has not attracted much attention, particularly when the silicon is bound to O-donors. The present paper reports thermodynamic data, obtained by calorimetric titration in solution in acetonitrile or benzene, for the formation of 1/1 adducts of a variety of bases with organosilicon acetates, $R_nSi(OCOMe)_{4-n}$ ($0 \leqslant n \leqslant 3$, R = Me or Ph) as Lewis acids. The methoxides, $Me_nSi(OMe)_{4-n}$ ($1 \leqslant n \leqslant 3$) were also studied, but showed no evidence of behaving as Lewis acids.

Experimental

Materials. Organosilicon acetates were prepared by slow addition of the corresponding chlorides to 30% excess of dry silver acetate, suspended in dry benzene or ether [8]. After stirring for one or two hours insoluble matter was filtered, the solvent evaporated and liquid residue fractionally distilled in vacuo. $Ph_3Si(OCOMe)$ however was obtained as a solid residue and was crystallised by dissolving in light petroleum and cooling the solution to −78°C. $Si(OCOMe)_4$ was also obtained as a solid residue and was recrystallised from acetic anhydride. Organosilicon methoxides were obtained from the chlorides and sodium methoxide in methanol, recovered by filtration of solids, evaporation of solvent and distillation in vacuo. The purity of all silicon compounds was confirmed by boiling or melting points and C and H analysis.

Liquid bases were purified by distillation and dried over anhydrous potassium carbonate; 2,2′-bipyridine and 1,10-phenanthroline were recrystallised from ethanol; pyridine-*N*-oxide was sublimed in vacuo. Phenanthroline was dehydrated by azeotropic distillation of benzene before making up solutions. Benzene for use as solvent was frozen, distilled and stored over calcium hydride; acetonitrile was dried over anhydrous sodium sulphate, distilled and stored over molecular sieve.

Calorimetry. Titrations were carried out in a LKB 8700 calorimeter using previously described techniques [9]. Briefly, a solution of the base was titrated into 100 ml of a solution of the silicon compound in the same solvent and the heat change measured after each incremental addition of titrant. The enthalpy of reaction was obtained from the extrapolated, integrated heat of reaction and the adduct formation constant, *K*, calculated at each point; the enthalpy was then refined iteratively to give constant values of *K* throughout the titration. Values of the enthalpy in tables are the mean of at least three determinations over the range of concentrations of the silicon compound indicated; uncertainties are mean deviations. Values of *K* are the mean of at least three determinations and uncertainties in *K* are the sum of the mean deviation and the average standard deviation in individual titrations. Uncertainties in ΔG^0 and ΔS^0 are derived.

All solutions throughout the calorimetric measurements were handled under dry nitrogen.

Results and discussion

Preliminary experiments showed that benzene, which we have previously used as preferred solvent for calorimetric studies of Lewis acid—base reactions, was not suitable for these silicon compounds; their reactions with bases in benzene solution were nearly always accompanied by the formation of traces of insoluble products and calorimetric measurements made in benzene had a poor level of reproducibility. It was found possible to overcome these problems by the use of polar solvents and after trials acetonitrile was selected, as being one of the least polar solvents acceptable. In this solvent all reactions were completed without precipitation and highly reproducible results were obtained. Parallel studies were carried out on many systems conductimetrically, but no evidence was found for the formation of ionic species, so that the only reactions which need to be considered are the formation of neutral adducts and disproportionation reactions where there are no ionic products. A small number of the most favorable systems were also studied in benzene solution, in which considerably higher adduct stabilities and rather more negative enthalpies of adduct formation were observed. In order to confirm that these differences were due to solvation effects and not to the formation of stoichiometric acetonitrile adducts, some of the most reactive silicon compounds were titrated in benzene solution with pure acetonitrile: in no case was any evidence found for the formation of acetonitrile adducts.

Calorimetric titrations were carried out of the three compounds $MeSi(OCOMe)_3$, $Me_2Si(OCOMe)_2$ and $Ph_2Si(OCOMe)_2$ with a wide range of bases and of $Si(OCOMe)$, $Ph_3Si(OCOMe)$ and $Me_3Si(OCOMe)$ with a more limited range; the last two compounds in particular were weaker Lewis acids and could only be titrated successfully with the most reactive bases. In all cases where titrations were successfully carried out the results could only be interpreted as representing the formation of 1/1 adducts:

$$R_nSi(OCOMe)_{4-n} + B \rightleftharpoons R_nSi(OCOMe)_{4-n}B$$

in which the silicon atom has a coordination number of five. Complete details of thermodynamic data for these systems are given in Tables 1—5.

Although most adducts are of only moderate stability and some, such as

TABLE 1

THERMODYNAMIC DATA FOR FORMATION OF 1/1 ADDUCTS OF BASES WITH $Si(OCOMe)_4$ IN ACETONITRILE SOLUTION AT 30°C (K in l mol^{-1}; ΔH^0, ΔG^0 in kJ mol^{-1}; ΔS^0 in J K^{-1} mol^{-1}; [Si] in mmol l^{-1})

Base	[Si]	K	$-\Delta H^0$	$-\Delta G^0$	$-\Delta S^0$
$BuNH_2$	2.7—4.5	64 ± 5	185.6 ± 0.7	10.5 ± 0.3	578 ± 3
$CxNH_2$ [a]	1.4—2.1	58 ± 2	171.8 ± 6.5	10.2 ± 0.2	533 ± 22
Et_2NH	1.8—3.6	130 ± 14	187.3 ± 8.3	12.3 ± 0.3	558 ± 28
Piperidine	1.1—1.7	198 ± 9	187.7 ± 3.6	13.3 ± 0.2	576 ± 13
Et_3N	1.8—4.5	102 ± 5	154.7 ± 2.0	11.7 ± 0.2	472 ± 7
tmed	3.6—5.3	76 ± 4	111.7 ± 1.1	10.9 ± 0.2	333 ± 4
$PhCH_2NH_2$	3.6—5.3	20.1 ± 0.7	109.3 ± 2.1	7.6 ± 0.2	336 ± 8
Pyridine	5.0—8.0	2.4 ± 0.1	80.0 ± 2.8	2.2 ± 0.2	257 ± 9
4-mepy	4.0—8.0	3.5 ± 0.1	84.4 ± 0.3	3.2 ± 0.1	268 ± 2
py-NO	6.0—8.0	11.8 ± 0.4	57.5 ± 1.4	6.2 ± 0.2	169 ± 5
tmed [b]	2.0—5.0	ca. 120	ca. 120		
$PhCH_2NH_2$ [b]	2.0—5.0	ca. 300	ca. 102		

[a] Cyclohexylamine. [b] In benzene solution.

TABLE 2

THERMODYNAMIC DATA FOR FORMATION OF 1/1 ADDUCTS OF BASES WITH $MeSi(OCOMe)_3$ IN ACETONITRILE SOLUTION AT 30°C (K in l mol^{-1}; ΔH^0, ΔG^0 in kJ mol^{-1}; ΔS^0 in J K^{-1} mol^{-1}; [Si] in mmol l^{-1}

Base	[Si]	K	$-\Delta H^0$	$-\Delta G^0$	$-\Delta S^0$
$BuNH_2$	2.5—4.6	57 ± 2	134.7 ± 1.7	10.2 ± 0.1	411 ± 6
i-$BuNH_2$	3.4—6.4	47 ± 2	124.6 ± 2.6	9.7 ± 0.1	379 ± 9
s-$BuNH_2$	2.1—4.3	40 ± 2	137.7 ± 4.4	9.3 ± 0.2	424 ± 15
t-$BuNH_2$	1.1—2.1	50 ± 5	141.0 ± 0.6	9.9 ± 0.3	433 ± 3
$CxNH_2$	1.5—2.4	47 ± 2	133.3 ± 0.7	9.7 ± 0.1	408 ± 3
Et_2NH	2.7—5.4	139 ± 5	130.0 ± 3.5	12.4 ± 0.1	388 ± 12
Bu_2NH	1.8—3.6	119 ± 7	124.0 ± 1.9	12.0 ± 0.2	369 ± 7
Piperidine	2.1—4.3	168 ± 7	141.3 ± 3.0	12.9 ± 0.2	424 ± 10
Et_3N	3.6—5.4	106 ± 5	114.3 ± 2.5	11.8 ± 0.2	338 ± 9
tmed	1.9—5.6	85 ± 3	84.7 ± 1.5	11.2 ± 0.1	243 ± 5
$PhCH_2NH_2$	2.7—4.5	14.5 ± 0.4	92.9 ± 3.4	6.7 ± 0.2	284 ± 12
Pyridine	5.6—9.4	2.4 ± 0.1	47.6 ± 1.8	2.2 ± 0.2	150 ± 6
4-mepy	6.9—9.4	3.5 ± 0.1	54.5 ± 0.7	3.1 ± 0.1	169 ± 3
2-mepy	3.4—6.4	2.9 ± 0.1	58.0 ± 1.0	2.7 ± 0.1	183 ± 3
py-NO	6.3—8.8	10.5 ± 0.2	43.9 ± 1.0	5.9 ± 0.1	125 ± 4

those with pyridine, quite unstable, their enthalpies of formation are in many instances very large. Enthalpies of formation of the adducts with aliphatic amines increase by about 50 kJ mol^{-1} for each replacement of Me or Ph by acetate; extrapolation back to R_4Si would give positive enthalpies of adduct formation, consistent with the observation that R_4Si do not exhibit Lewis acidity. Replacement of Me by Ph leads in most instances to a small increase in the enthalpy of adduct formation (average 8 kJ mol^{-1}), but has no significant effect on the adduct stabilities.

TABLE 3

THERMODYNAMIC DATA FOR FORMATION OF 1/1 ADDUCTS OF BASES WITH $Me_2Si(OCOMe)_2$ IN ACETONITRILE SOLUTION AT 30°C (K in l mol^{-1}; ΔH^0, ΔG^0 in kJ mol^{-1}; ΔS^0 in J K^{-1} mol^{-1}; [Si] in mmol l^{-1})

Base	[Si]	K	$-\Delta H^0$	$-\Delta G^0$	$-\Delta S^0$
$BuNH_2$	1.6—4.0	46 ± 3	79.1 ± 1.2	9.6 ± 0.2	229 ± 4
i-$BuNH_2$	6.4—10.7	35 ± 3	92.6 ± 2.1	8.9 ± 0.3	267 ± 7
s-$BuNH_2$	1.6—4.0	42 ± 2	87.4 ± 3.2	9.4 ± 0.2	258 ± 11
t-$BuNH_2$	2.1—3.2	58 ± 4	90.1 ± 2.6	10.2 ± 0.3	263 ± 10
$CxNH_2$	1.4—4.1	52 ± 3	82.0 ± 4.4	10.0 ± 0.2	238 ± 15
Et_2NH	4.3—8.5	134 ± 2	83.5 ± 3.5	12.3 ± 0.1	235 ± 12
Bu_2NH	4.0—6.0	116 ± 2	89.1 ± 1.7	12.0 ± 0.1	254 ± 6
Piperidine	5.0—8.0	152 ± 11	85.4 ± 5.0	12.7 ± 0.3	240 ± 17
Et_3N	4.6—7.2	109 ± 5	76.8 ± 1.4	11.8 ± 0.2	214 ± 5
tmed	6.0—10.0	70 ± 4	56.3 ± 2.7	10.7 ± 0.2	151 ± 9
$PhCH_2NH_2$	4.0—7.0	17.5 ± 0.5	52.3 ± 1.3	7.2 ± 0.1	149 ± 4
Pyridine	9.0—12.0	2.2 ± 0.2	31.5 ± 1.8	2.0 ± 0.3	97 ± 6
4-mepy	9.0—13.0	3.1 ± 0.2	33.5 ± 0.4	2.8 ± 0.2	108 ± 2
2-mepy	8.5—12.8	2.8 ± 0.2	34.7 ± 0.7	2.6 ± 0.3	106 ± 3
py-NO	7.5—10.2	11.7 ± 0.1	28.6 ± 0.2	6.2 ± 0.1	74 ± 1
$BuNH_2$ [a]	3.6—6.4	351 ± 48	118.5 ± 3.4	14.8 ± 0.5	342 ± 12

[a] In benzene solution.

TABLE 4

THERMODYNAMIC DATA FOR FORMATION OF 1/1 ADDUCTS OF BASES WITH $Ph_2Si(OCOMe)_2$ IN ACETONITRILE SOLUTION AT 30 C (K in l mol^{-1}; ΔH^0, ΔG^0 in kJ mol^{-1}; ΔS^0 in J K^{-1} mol^{-1}; [Si] in mmol l^{-1})

Base	[Si]	K	$-\Delta H^0$	$-\Delta G^0$	$-\Delta S^0$
$BuNH_2$	4.2—6.0	54 ± 5	101.8 ± 0.5	10.1 ± 0.3	303 ± 6
$i\text{-}BuNH_2$	3.4—5.7	46 ± 3	78.5 ± 3.4	9.6 ± 0.2	227 ± 11
$s\text{-}BuNH_2$	3.0—4.7	41 ± 3	95.1 ± 1.6	9.4 ± 0.2	283 ± 6
$t\text{-}BuNH_2$	2.0—3.0	466 ± 2	99.9 ± 4.0	9.6 ± 0.2	298 ± 13
$CxNH_2$	2.0—4.0	41 ± 1	89.2 ± 2.5	9.4 ± 0.1	263 ± 9
Et_2NH	3.6—6.1	154 ± 10	88.3 ± 2.1	12.7 ± 0.3	249 ± 8
Bu_2NH	1.8—4.3	123 ± 6	88.3 ± 3.2	12.1 ± 0.2	251 ± 11
Piperidine	3.0—5.0	202 ± 15	95.8 ± 2.5	13.4 ± 0.3	272 ± 9
Et_3N	3.0—5.5	136 ± 11	75.4 ± 1.9	12.4 ± 0.3	208 ± 7
tmed	2.6—4.3	66 ± 2	64.9 ± 0.8	10.6 ± 0.1	179 ± 3
$PhCH_2NH_2$	3.0—5.0	17.0 ± 0.6	50.5 ± 2.5	7.1 ± 0.2	143 ± 8
Pyridine	7.0—10.6	2.2 ± 0.1	41.6 ± 2.1	1.9 ± 0.2	131 ± 7
4-mepy	8.3—14.0	3.0 ± 0.1	44.9 ± 0.3	2.8 ± 0.1	139 ± 2
2-mepy	5.0—10.0	2.1 ± 0.1	44.1 ± 1.4	1.9 ± 0.2	139 ± 5
py-NO	5.0—12.0	12.9 ± 0.5	23.1 ± 1.6	6.4 ± 0.2	55 ± 5

In spite of increasing enthalpies of adduct formation as acetate replaces Me or Ph, adduct stabilities are not affected in the same way: whatever base is used there is almost no change in adduct stabilities from $Si(OCOMe)_4$ to $Me_2Si(OCOMe)_2$, but adducts of $Me_3Si(OCOMe)$, which have by far the smallest enthalpies of formation, are significantly the most stable. Evidently replacement by acetate produces a considerable inductive effect, reflected in the increased enthalpy of adduct formation, but this is counterbalanced by a steric effect, particularly when there is more than one acetate group in the molecule. Steric resistance to adduct formation must occur close to the silicon atom as there is no evidence for reduced adduct stability or lower enthalpy of adduct formation with t-butylamine or 2-methylpyridine. The type of steric effect is probably that referred to by Brown [10] as B-strain; this implies that there is little likelihood of extending the coordination number of the silicon atom in these compounds beyond five, however large the additional bond energies might be. This

TABLE 5

THERMODYNAMIC DATA FOR FORMATION OF 1 : 1 ADDUCTS OF BASES WITH $R_3Si(OCOMe)$ IN ACETONITRILE SOLUTION AT 30°C (K in l mol^{-1}; ΔH^0, ΔG^0 in kJ mol^{-1}) ΔS^0 in J K^{-1} mol^{-1}; [Si] in mmol l^{-1})

Base	R	[Si]	K	$-\Delta H^0$	$-\Delta G^0$	$-\Delta S^0$
$BuNH_2$	Me	2.4—3.7	97 ± 3	30.0 ± 1.3	11.5 ± 0.1	61 ± 4
$CxNH_2$	Me	1.8—3.3	127 ± 8	22.9 ± 0.9	12.2 ± 0.2	35 ± 3
Et_2NH	Me	4.5—5.6	307 ± 22	34.8 ± 1.5	14.4 ± 0.3	67 ± 5
	Ph	2.7—5.9	252 ± 13	29.9 ± 0.3	13.9 ± 0.2	53 ± 2
Piperidine	Me	4.5—6.8	407 ± 29	35.6 ± 0.9	15.1 ± 0.3	68 ± 4
	Ph	1.0—3.5	406 ± 20	37.9 ± 1.0	15.1 ± 0.2	75 ± 4
Et_3N	Me	5.3—6.8	146 ± 10	35.4 ± 1.2	12.6 ± 0.3	75 ± 4
	Ph	1.5—7.3	154 ± 6	28.7 ± 1.6	12.7 ± 0.2	53 ± 5

is supported by the failure of Si(OCOMe)$_4$ to add more than one base molecule, despite the very large enthalpy changes which might be expected. There is also some other evidence in the data obtained:

The base *N,N,N',N'*-tetramethyl-1,2-diaminoethane (tmed) forms 1/1 adducts with these silicon compounds, in which it might be expected that both N atoms would be coordinated, giving a chelate ring with six-coordinate silicon; this is the normal behaviour of this base with other acceptor atoms. The enthalpies of formation of these 1/1 adducts, however, are less than those of adducts with triethylamine and so are their stabilities, showing clearly that tmed is only unidentate. The heterocyclic bases 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) also usually behave as bidentate ligands, forming chelate complexes of enhanced stability, but neither of these bases gave any evidence of adduct formation at all; their adducts, if any, are much less stable than those of pyridine and again show clearly the impossibility of forming six-coordinate compounds in this series.

Heterocyclic bases and pyridine-*N*-oxide form much less stable adducts with all these silicon compounds than do the alkyl amines; this is clearly due to lower enthalpies of adduct formation; benzylamine comes between these two groups. These variations can be associated with the "hard" nature of the silicon centre and its similarity in this respect to hydrogen is shown by the broad correlation of pK_a of the base and the free energy of adduct formation. This is shown in Fig. 1 for adducts of Me$_2$Si(OCOMe)$_2$ and analogous results are obtained for the other compounds.

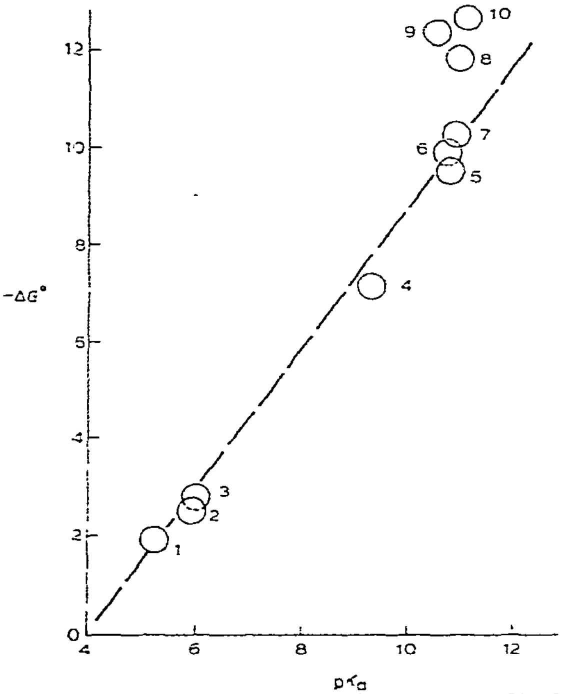

Fig. 1. Free energy of formation of adducts with Me$_2$Si(OCOMe)$_2$ (kJ mol^{-1}) and pK_a of base [12]. 1, Pyridine; 2, 2-mepy; 3, 4-mepy; 4, PhCH$_2$NH$_2$; 5, BuNH$_2$; 6, Cyclohexylamine; 7, t-BuNH$_2$; 8, NEt$_3$; 9, Et$_2$NH; 10, piperidine.

TABLE 6

THERMODYNAMIC DATA FOR FORMATION OF 1/1 ADDUCTS OF BASES WITH $Ph_2Si(OCOMe)_2$ IN ACETONITRILE AND $Ph_2Sn(OCOMe)_2$ IN BENZENE SOLUTION AT 30°C (K in l mol^{-1}, ΔH^0 in kJ mol^{-1})

Base	$Ph_2Si(OCOMe)_2$		$Ph_2Sn(OCOMe)_2$ [11]	
	K	$-\Delta H^0$	K	$-\Delta H^0$
Pyridine	2.2 ± 0.1	41.6 ± 2.1	19 ± 1	27.6 ± 0.5
4-mepy	3.0 ± 0.1	44.9 ± 0.3	49 ± 5	30.8 ± 0.5
py-NO	13 ± 1	23.1 ± 1.6	70 ± 5	30.8 ± 1.2
Et_3N	136 ± 11	75.4 ± 1.9	117 ± 7 [a]	22.1 ± 0.3 [a]
tmed	66 ± 2	64.9 ± 0.8	82 ± 8	22.9 ± 1.1

[a] New value not included in ref. 11.

Comparison of the Lewis acidity of corresponding silicon and tin compounds is complicated by change of solvent; available data for addition of bases to organotin acetates are in benzene, whereas most of the present results are in acetonitrile. The small number of data included here for reactions of organosilicon compounds in benzene solution make some valid comparisons possible; several other silicon compounds were also studied in benzene, but the results are not reported because of low reliability. These and the reported results show, however, that the change of solvent from acetonitrile to benzene leads to small increases in enthalpy of adduct formation and considerable increase in adduct stabilities. Table 6 compares values for the enthalpy of formation and stability of adducts of selected bases with $Ph_2Si(OCOMe)_2$ in acetonitrile and $Ph_2Sn(OCOMe)_2$ in benzene [11].

Allowing for increased stabilities and enthalpies of formation of the adducts of $Ph_2Si(OCOMe)_2$ in benzene, it is clear that the main difference between the two series is the much greater enthalpy of formation of adducts of N-bases with the silicon compound. This may probably be attributed to a simple inductive effect arising from the smaller size of the silicon atom.

The broad conclusion can be drawn that when the compounds $R_nSi(OCOMe)_{4-n}$ $(0 \leqslant n \leqslant 3)$ behave as Lewis acids the coordination number of the silicon atom does not exceed five. Adduct stabilities are not much different from those of corresponding organotin compounds, but the enthalpies of formation of the adducts with silicon compounds are considerably greater. This underlines the extremely important role of the entropy term in determining the strength of Lewis acids.

Acknowledgements

We are grateful to the Australian Research Grants Committee for supporting this work. One of us (B.A.R.) acknowledges a Colombo Plan fellowship.

References

1 F. Klanberg and E.L. Muetterties, Inorg. Chem., 7 (1968) 155.
2 C. Eaborn, "Organosilicon Compounds", p. 92, Butterworth, London (1960) and refs. therein.