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Bonding studies on zinc, cadmium, and mercury alkyls and amides, $Zn(CH_2EMe_3)_2$ (E = C or Si) and $M[N(SiMe_3)_2]_2$ (M = Zn, Cd, or Hg). Heats of hydrolysis, standard heats of formation, and Zn–C and M–N (M = Zn, Cd, or Hg) bond energy terms *

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Abstract

Calorimetric measurements have been carried out on the heats of hydrolysis of the homoleptic zinc alkyls $Zn(CH_2EMe_3)_2$ (E = C or Si) and bis(trimethylsilyl)-amides $M[N(SiMe_3)_2]_2$ (M = Zn, Cd, or Hg) at 25 ± 0.01° C in aqueous hydrochloric (1 *M*; for the Zn compounds) or sulphuric (0.5 *M*; for the amides) acid. Using appropriate subsidiary data, values were derived for the standard enthalpies of formation ΔH_f^0 of the following liquid compounds: $Zn(CH_2CMe_3)_2$, 175 ± 14; $Zn(CH_2SiMe_3)_2$, 410 ± 19; $Zn[N(SiMe_3)_2]_2$, 951 ± 9 (in eq. HCl) or 963 ± 9 (in aqueous H_2SO_4); $Cd[N(SiMe_3)_2]_2$, 85 ± 21; and $Hg[N(SiMe_3)_2]_2$, 834 ± 9 kJ mol^{-1}. Using these data, and calculated enthalpies of vaporization, led (via $\Delta H_f^0(g)$) to the following relative M–C and M–N bond energy terms ($\bar{E}$): Zn–C (CH_2CMe_3), 157; Zn–C (CH_2SiMe_3), 195; Zn–N, 203 (from HCl experiments); Zn–N, 209 (from the H_2SO_4 experiments); Cd–N, 144; and Hg–N, 108 kJ mol^{-1}.

Introduction

Two of us (M.F.L. and J.B.P.) have collaborated on problems concerning (a) compounds of boron and other group 13–15 elements [1], and (b) some transition metal alkyls, dialkylamides, and bis(trimethylsilyl)amides [2]. The objective was to

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* Dedicated to Professor Colin Eaborn, in recognition of his important contributions to organometallic chemistry. M.F.L. and J.B.P., his friends and colleagues, wish also to pay tribute to his pivotal role in creating the flourishing and happy School of Chemistry and Molecular Sciences in The University of Sussex.

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contribute to an understanding of the bonding in such molecules: the methods used involved calorimetry, mass spectrometry, He(I) photoelectron spectroscopy, and NMR spectroscopy. Experiments were designed so as to provide data on (i) standard enthalpies of formation, (ii) ΔG, ΔH, and ΔS for a variety of reactions, and (iii) valence ionisation energies of parent molecules and appearance potentials of fragment ions. In some instances, especially in the context of (iii), molecular orbital calculations were presented.

The present paper deals with calorimetric data on alkyls and bis(trimethylsilyl)-amides of bivalent zinc, cadmium, and mercury, MX_2. We had three principal aims. The first was to study trends in mean M–X bond energies ($\bar{E}$) as a function of the atomic number of M. The second was to compare $\bar{E}$(M–C) and $\bar{E}$(M–N). Finally, we sought to determine whether the mean M–C bond energy in the linear ZnR_2 was sensitive to the nature of R in the context of a comparison between CH_2EMe_3 (E = C or Si) ligands.

Our earlier thermochemical studies have provided enthalpies of formation of (i) $(Me_3Si)_nX$ (**1**) ($n = 1$, with X = Cl, Br, OH, OBu^n, NHMe, or NMe_2; $n = 2$, with X = NH or NMe; and $n = 3$, with X = N) [3], (ii) Me_3SiOEt, $(Me_3Si)_2O$ and some Ge^{IV} and Sn^{IV} analogues of **1** [4], and (iii) the d^0 complexes $[M'X'_4]$ (M′ = Ti, Zr, or Hf; X′ = Cl, CH_2CMe_3, CH_2SiMe_3, NMe_2, NEt_2, or $OCHMe_2$) [5]. Solution calorimetric techniques used were based on measurements of enthalpies of hydrolysis in aqueous acid for (i) or (ii), or of alcoholysis ($CHMe_2OH$) for (iii). The overall conclusions relevant to the present work were as follows (for constant X) (a) $\bar{E}(C–X) > \bar{E}(Si–X) > \bar{E}(Ge–X) > \bar{E}(Sn–X)$, (b) $\bar{E}(Hf–X) \geqslant \bar{E}(Zr–X) \gg \bar{E}(Ti–X)$, (c) $\bar{E}(M''–NR_2) > \bar{E}(M''–Alk)$ (M″ = Si, Ge, Sn, Ti, Zr, or Hf), and (d) $M–CH_2CMe_3$ (M = Ti, Zr, or Hf) bonds are considerably weaker than $M–CH_2R$ (M = Ti, Zr, or Hf; R = Ph or $SiMe_3$). From (a) and (b), we proposed the notion that a significant difference between a *d*-block and a *p*-block sub-group of metals is a reversal in progression in thermochemical bond strengths with increasing atomic number: increasing for the *d*-block elements, but decreasing for the *p*-block analogues [5,6]; related data along similar lines to (b) and (c), including on Nb^V, Ta^V, Mo^{VI}, and W^{VI} compounds, led to the same conclusion [7]. Heats of alcoholysis (Me_3COH) for thoracene(IV) complexes, $[Th(\eta\text{-}C_5Me_5)_2X_2]$, have been determined, whence the trends (c) and (d) were derived also for this series; $\bar{D}$(Th–X) was found to decrease in the sequence X = H ≈ NR_2 > Me ≈ CH_2SiMe_3 > CH_2CMe_3 [8]. In a heteroleptic series, such as the latter, there is more uncertainty than in the homoleptic counterpart MX_n to apportion energy specifically to M–X bonds [5].

Results and discussion

The enthalpy of hydrolysis of ZnR_2 or $M[N(SiMe_3)_2]_2$ ($-\Delta H_{obs}$) data are summarised in the first column of Table 1, each observed value being the mean of at least five separate measurements, using either 1 *M* hydrochloric acid or 0.5 *M* sulphuric acid as the hydrolysing medium.

The enthalpies of formation of the products in solution are not known precisely: hence an extensive series of enthalpy of solution or mixing measurements was made to derive enthalpies of reaction with respect to well-characterised materials as products. In particular, since zinc chloride is a hygroscopic material which is very difficult to purify, the heptahydrate of zinc sulphate was used in the comparison

Table 1
Heats (kJ mol^{-1}) of hydrolysis, formation, and vaporisation of zinc, cadmium, and mercury alkyls and amides, and mean M–C and M–N bond energy terms (kJ mol^{-1})

Compound	$-\Delta H_{obs}$ [a]	$-\Delta H^0_f$(l)	ΔH_v [b]	$-\Delta H^0_f$(g)	$\bar{E}$(M–R)	Bond
$Zn(CH_2CMe_3)_2$(l)	317.6 ± 14	174.9 ± 14	51.8 ± 10	123.0 ± 17	157	Zn–C
$Zn(CH_2SiMe_3)_2$(l)	276.2 ± 12	409.7 ± 19	54.4 ± 10	355.3 ± 21	195	Zn–C
$Zn[N(SiMe_3)_2]_2$(l)	520.3 ± 4	951.2 ± 9	68.2 ± 10	883.1 ± 13	203	Zn–N
$Zn[N(SiMe_3)_2]_2$(l) [c]	535.9 ± 7	962.8 ± 9	68.2 ± 10	894.7 ± 13	209	Zn–N
$Cd[N(SiMe_3)_2]_2$(l) [c]	566.6 ± 20	853.8 ± 21	70.3 ± 10	783.5 ± 23	144	Cd–N
$Hg[N(SiMe_3)_2]_2$(l) [c]	337.3 ± 4	833.7 ± 9	71.5 ± 10	762.1 ± 13	108	Hg–N

[a] Uncertainties equal to twice the standard deviation of the mean of at least five separate measurements, except for $Cd[N(SiMe_3)_2]_2$, where shortage of material allowed only two measurements with the values 558.48 and 574.77 kJ mol^{-1}, and the error is estimated. [b] Values calculated from boiling point using the equation: $\Delta H_v = [5.0 + 0.041(T_b - 273)] \times 4.184$ kJ mol^{-1}, where T_b is the boiling point (E. Wadso, Acta Chem. Scand., 20 (1966) 544). These boiling points are not known accurately (Table 7); hence the large estimated errors. [c] Values in 0.5 *M* H_2SO_4 solution; the other data refer to 0.1 *M* HCl solution.

experiments. The subsidiary measurements on enthalpies of solution and mixing are summarised in Table 2, the quantities of materials used being such that the final solution produced had a similar composition to that obtained in the hydrolysis measurements. No detectable enthalpy change was observed for the mixing of either tetramethylsilane or hexamethyldisiloxane with the aqueous acids. Hydrolysis of $Zn(CH_2CMe_3)_2$ gave CMe_4 in unknown proportions of liquid and gaseous phase. An appropriate correction was made by breaking bulbs of liquid CMe_4 into hydrochloric acid, the enthalpy change of 17.4 kJ mol^{-1} corresponding mainly to vaporisation of the material.

Evidence for complete and rapid hydrolysis under our calorimeter conditions of the zinc dialkyl, ZnR_2, or the amide, $M[N(SiMe_3)_2]_2$ (M = Zn, Cd, or Hg), to release quantitatively the $\bar{R}$ or $\bar{N}(SiMe_3)_2$ ligand as RH or $(Me_3Si)_2O$, was demonstrated by (i) the formation of a water-immiscible layer of RH or $(Me_3Si)_2O$ in the calorimeter (Me_3SiOH is water-soluble), (ii) the rate of heat output, (iii) the negligible heat of solution in aqueous acid of RH or $(Me_3Si)_2O$ and the measured ΔH_{obs}

Table 2
Subsidiary ΔH values (kJ mol^{-1}) measured under various experimental conditions [a]

Substance	Aqueous acid	ΔH_{obs} (kJ mol^{-1}) [b]
$ZnSO_4 \cdot 7H_2O$(c)	0.5 *M* H_2SO_4	22.6
$ZnSO_4 \cdot 7H_2O$(c)	1 *M* H_2SO_4	44.7
$[NH_4]_2[SO_4]$(c)	0.5 *M* H_2SO_4	22.5
$[NH_4]Cl$(c)	1 *M* HCl	16.6
CMe_4(l)	1 *M* HCl	17.4 [c]
$SiMe_4$(l)	1 *M* HCl	0.00
$(Me_3Si)_2O$(l)	0.5 *M* H_2SO_4	0.00
$CdSO_4(\frac{8}{3}H_2O)$(c)	0.5 *M* H_2SO_4	−9.3
$HgSO_4$(c)	0.5 *M* H_2SO_4	−18.9

[a] To duplicate the composition produced in the hydrolysis reactions; see eq. 1 to 14. [b] The uncertainty on these measurements is < ±2 kJ mol^{-1}. [c] This corresponds mainly to vaporisation of CMe_4(l), see text.

for CMe_4(l) in 1 *M* HCl, and (iv) ^1H NMR experiments which simulated the calorimetric conditions.

Calculation of ΔH_f^0

The enthalpies of hydrolysis of $Zn(CH_2CMe_3)_2$ or $Zn(CH_2SiMe_3)_2$ correspond to the process of eq. 1, with $R = CH_2CMe_3$ or CH_2SiMe_3, respectively, except that for $Zn(CH_2CMe_3)_2$ the eliminated CMe_4 was a mixture of liquid and gas.

$$ZnR_2(l) + (100HCl + 5500H_2O)(l) = [Zn^{2+} + 98H^+ + 100Cl^- + 5500H_2O + 2RH](l) \quad (1)$$

The precise composition of the final solution is difficult to define, because of complex formation between Zn^{2+}, H_2O and Cl^- ions. However, appropriate measured data were selected (Table 2) so as to overcome this uncertainty. The relevant processes are given in eqs. 2, 3, and 4.

$$[Zn^{2+} + 98H^+ + 100Cl^- + 5500H_2O](l) + 2RH(l) = [Zn^{2+} + 98H^+ + 100Cl^- + 5500H_2O + 2RH](l) \quad (2)$$

$$ZnSO_4 \cdot 7H_2O(c) + [100HCl + 5603H_2O](l) = [Zn^{2+} + [SO_4]^{2-} + 100H^+ + 100Cl^- + 5610H_2O](l) \quad (3)$$

$$[H_2SO_4 + 110H_2O](l) + [Zn^{2+} + 98H^+ + 100Cl^- + 5500H_2O](l) = [Zn^{2+} + [SO_4]^{2-} + 100H^+ + 100Cl^- + 5610H_2O](l) \quad (4)$$

The enthalpy change for the processes of eq. 4 was measured by breaking bulbs containing ca. 0.5 cm^3 of 0.5 *M* sulphuric acid into 30 cm^3 of solution product from the hydrolysis reaction. Using $-\Delta H_{obs}$ for $Zn(CH_2EMe_3)_2$ ($\equiv ZnR_2$; E = C or Si) (Table 1) and appropriate data from Table 2, the enthalpy change ΔH_5 for the process of eq. 5 was obtained, according to eqs. a and b.

$$ZnR_2(l) + [100HCl + 5500H_2O](l) + [H_2SO_4 + 110H_2O](l) = ZnSO_4 \cdot 7H_2O(c) + [100HCl + 5603H_2O](l) + 2RH(l) \quad (5)$$

$$\Delta H_5 = \Delta H_1 - 2\Delta H_2 - \Delta H_3 + \Delta H_4 = -397.03 \pm 4.6 \text{ kJ mol}^{-1}, \text{ for } R = CH_2CMe_3 \quad (a)$$

$$\Delta H_5 = \Delta H_1 - 2\Delta H_2 - \Delta H_3 + \Delta H_4 = -320.85 \pm 3.35 \text{ kJ mol}^{-1}, \text{ for } R = CH_2SiMe_3 \quad (b)$$

Using $-\Delta H_5$ and relevant subsidiary data from Table 3 [4,5], the standard enthalpies of formation ($-\Delta H^0{}_f$(l)) of the zinc alkyls $Zn(CH_2EMe_3)_2$ (E = C or Si) were derived, Table 1. (The calculation includes an enthalpy of dilution of 1.46 kJ mol^{-1} for the process $(100HCl + 5500H_2O) = (100HCl + 5603H_2O)$).

The enthalpy of hydrolysis of $Zn[N(SiMe_3)_2]_2$ in hydrochloric acid corresponds to the process of eq. 6.

$$Zn[N(SiMe_3)_2]_2(l) + [100HCl + 5500H_2O](l) = [Zn^{2+} + 2[NH_4]^+ + 96H^+ + 100Cl^- + 5498H_2O + 2(Me_3Si)_2O](l) \quad (6)$$

From appropriate heat of solution measurements selected from Table 2, the heats of reactions according to eqs. 7 and 8 (ΔH_7 and ΔH_8) were derived. Equation 9 was found to correspond to a negligible enthalpy change; likewise the enthalpy of mixing of $(Me_3Si)_2O$ with the aqueous acid solution was shown to be zero.

$$ZnSO_4 \cdot 7H_2O(c) + [98HCl + 5601H_2O](l) = \left[Zn^{2+} + [SO_4]^{2-} + 98H^+ + 98Cl^- + 5608H_2O\right](l) \quad (7)$$

$$2[NH_4]Cl(c) + \left[Zn^{2+} + [SO_4]^{2-} + 98H^+ + 98Cl^- + 5608H_2O\right](l) = \left[Zn^{2+} + 2[NH_4]^+ + [SO_4]^{2-} + 98H^+ + 100Cl^- + 5608H_2O\right](l) \quad (8)$$

$$[H_2SO_4 + 110H_2O](l) + \left[Zn^{2+} + 2[NH_4]^+ + 96H^+ + 100Cl^- + 5498H_2O\right](l) = \left[Zn^{2+} + 2[NH_4]^+ + [SO_4]^{2-} + 98H^+ + 100Cl^- + 5608H_2O\right](l) \quad (9)$$

Using $-\Delta H_{obs}$ (Table 1) and selected data from Table 2 the enthalpy change for the process according to eq. 10 (ΔH_{10}) was obtained, eq. c.

$$Zn[N(SiMe_3)_2]_2(l) + [100HCl + 5500H_2O](l) + [H_2SO_4 + 110H_2O](l) = ZnSO_4 \cdot 7H_2O(c) + 2[NH_4]Cl(c) + 2(Me_3Si)_2O(l) + [98HCl + 5601H_2O](l) \quad (10)$$

$$\Delta H_{10} = \Delta H_6 - \Delta H_7 - 2\Delta H_8 + \Delta H_9 = -598.2 \pm 1.5 \text{ kJ mol}^{-1} \quad (c)$$

From ΔH_{10} and appropriate subsidiary data from Table 3 (including an enthalpy of dilution of HCl of 2.93 kJ mol^{-1}), the standard enthalpy of formation ($-\Delta H_f^0(l)$) of $Zn[N(SiMe_3)_2]_2$ was obtained, Table 1.

Table 3
Subsidiary data for calculation of ΔH^0_f (kJ mol^{-1}) [a]

Compound	ΔH^0_f (kJ mol^{-1})
$H_2O(l)$	-285.85 ± 0.04 [b]
$[NH_4]Cl(c)$	-315.18 ± 0.29 [b]
$[NH_4]_2[SO_4](c)$	-1182.65 ± 0.08 [b]
$ZnSO_4 \cdot 7H_2O(c)$	-3077.75 [c]
$CdSO_4(\frac{8}{3}H_2O)(c)$	-1729.54 ± 0.84 [d]
$HgSO_4(c)$	-707.51 [c]
$CMe_4(l)$	-189.77 ± 0.42 [e]
$(Me_3Si)_2O(l)$	-814.62 ± 5.44 [e]
$HCl(55H_2O)$	-165.39 ± 0.105 [b]
$H_2SO_4(110H_2O)$	-888.18 ± 0.042 [b]
$SiMe_4(l)$	-271.54 ± 10.04 [e]

[a] Enthalpies of dilution of HCl and H_2SO_4 taken from the reference in footnote *c*. [b] V.B. Parker, D.D. Wagman, and D. Garvin, Selected Thermochemical Data Compatible with CODATA Recommendations, NBSIR 75-968, Office of Standard Reference Data, National Bureau of Standards, Washington, D.C. 20234. [c] D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey, and R.H. Schumm, Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Technical Note 270-3,4, U.S. Government Printing Office, Washington, D.C. [d] Tentative Set of Key Values for Thermodynamics, Part VI, CODATA, Special Report No. 4, March 1977. [e] J.B. Pedley and J. Rylance, Sussex-N.P.L. Computer Analysed Thermochemical Data, University of Sussex, Brighton, 1977.

The enthalpy of hydrolysis of $Zn[N(SiMe_3)_2]_2$ was also measured in 1 *M* sulphuric acid solution, the process being given by eq. 11.

$$Zn\left[N(SiMe_3)_2\right]_2(l) + [50H_2SO_4 + 5500H_2O](l)$$
$$= \left[Zn^{2+} + 2[NH_4]^+ + 96H^+ + 50[SO_4]^{2-} + 5498H_2O + 2(Me_3Si)_2O\right](l) \quad (11)$$

The corresponding enthalpies of solution and mixing are given by eqs. 12 and 13.

$$ZnSO_4 \cdot 7H_2O(c) + [48H_2SO_4 + 5491H_2O](l)$$
$$= \left[Zn^{2+} + 49[SO_4]^{2-} + 96H^+ + 5498H_2O\right](l) \quad (12)$$

$$[NH_4]_2[SO_4](c) + \left[Zn^{2+} + 49[SO_4]^{2-} + 96H^+ + 5498H_2O\right](l)$$
$$= \left[Zn^{2+} + 2[NH_4]^+ + 50[SO_4]^{2-} + 96H^+ + 5498H_2O\right](l) \quad (13)$$

The heats of these processes (ΔH_{12} and ΔH_{13}) were calculated by selecting appropriate experimental data from Table 2. Hence from $-\Delta H_{obs}$ (Table 1), ΔH_{12} and ΔH_{13}, the enthalpy change ΔH_{14} for the process of eq. 14 was obtained, eq. d.

$$Zn\left[N(SiMe_3)_2\right]_2(l) + [50H_2SO_4 + 5500H_2O](l) = ZnSO_4 \cdot 7H_2O(c)$$
$$+ [NH_4]_2[SO_4](c) + 2(Me_3Si)_2O(l) + [48H_2SO_4 + 5491H_2O](l) \quad (14)$$

$$\Delta H_{14} = \Delta H_{11} - \Delta H_{12} - \Delta H_{13} = -581.1 \pm 0.8 \text{ kJ mol}^{-1} \quad (d)$$

From ΔH_{14}, the enthalpy of dilution of the sulphuric acid solution (2.30 kJ mol^{-1}), and using subsidiary data from Table 3, a value of 962.8 ± 9 kJ mol^{-1} was derived for the enthalpy of formation ($\Delta H^0{}_f(l)$) for $Zn[N(SiMe_3)_2]_2(l)$, in satisfactory agreement with the value obtained from hydrolysis in hydrochloric acid, 951.2 ± 9 kJ mol^{-1}, Table 1.

The standard enthalpies of formation, $\Delta H^0{}_f(l)$ of $Cd[N(SiMe_3)_2]_2(l)$ and $Hg[N(SiMe_3)_2]_2(l)$ (Table 1) were obtained in a similar way relative to the standard enthalpies of formation of $CdSO_4 \cdot \frac{8}{3}H_2O(c)$ and $HgSO_4(c)$. Enthalpy of solution values were found to be unaffected by changing from a solution containing Zn^{2+} to a solution containing Cd^{2+} or Hg^{2+}.

Calculation of bond energies

The strength of the metal-to-carbon or metal-to-nitrogen bonds can be represented by mean bond dissociation energies $\bar{D}$ (with $2\bar{D}$ being the enthalpy change for the process $MX_2(g) \rightarrow M(g) + 2\dot{X}(g)$) or by bond energy term values ($\bar{E}$). Since reliable standard enthalpies of formation are not known for all the radicals $\dot{X}$ concerned (especially $\dot{N}(SiMe_3)_2(g)$), relative bond energies as defined by $\bar{E}$ have been calculated.

The enthalpy change ΔH_{15} for the gas phase reaction of eq. 15 is given by eq. e or f (where M = Zn, Cd, or Hg; R = CH_2CMe_3, CH_2SiMe_3, or $N(SiMe_3)_2$)

$$MR_2(g) + 2H(g) = M(g) + 2RH(g) \quad (15)$$

$$\Delta H_{15} = \Delta H_f^0 M(g) + 2\Delta H_f^0 RH(g) - \Delta H_f^0 MR_2(g) - 2\Delta H_f^0 H(g) \quad (e)$$

$$\Delta H_{15} = 2\bar{E}(M\text{–}R) - 2\bar{E}(R\text{–}H) \quad (f)$$

The enthalpies of formation, $\Delta H_f^0(g)$, of the gaseous compounds MR_2 were obtained using enthalpies of vaporization ΔH_v calculated from their boiling points

Table 4
Subsidiary ΔH^0(g) data for calculation of bond energy terms

Species (g)	ΔH^0(g) (kJ mol^{-1})
H(g)	217.99 ± 0.084 [a]
Zn(g)	130.42 ± 0.020 [a]
Cd(g)	111.55 ± 0.59 [b]
Hg(g)	61.38 ± 0.042 [b]
NH_3(g)	-45.94 ± 0.35 [b]
CH_4(g)	-74.85 ± 0.29 [c]
CMe_4(g)	-167.40 ± 0.71 [c]
$SiMe_4$(g)	-245.60 ± 10.04 [c]
$HN(SiMe_3)_2$(g)	-476.56 ± 5.86 [c]
C(g)	716.68 ± 0.46 [a]
N(g)	472.68 ± 0.40 [a]

[a] V.B. Parker, D.D. Wagman, and D. Garvin, Selected Thermochemical Data Compatible with CODATA Recommendations, NBSFR 75-968, Office of Standard Reference Data, National Bureau of Standards, Washington, D.C. 20234. [b] Tentative Set of Key Values for Thermodynamics, Part VI, CODATA, Special Report No. 4, March, 1977. [c] J.B. Pedley, and J. Rylance, Sussex-N.P.L. Computer Analysed Thermochemical Data, University of Sussex, Brighton, 1977.

(Table 7) and using Wadso's equation (Table 1). The latter has been shown to give excellent agreement with experiment (to ± 2–3 kJ mol^{-1}) for other dialkyls of zinc, using data from ref. 9.

In eq. f, the mean bond energies $\bar{E}$(R–H) are assumed to have the average values in CH_4 and NH_3 as appropriate to the groups R. The bond energy terms $\bar{E}$(C–H) and $\bar{E}$(N–H) were calculated to be 415.9 kJ mol^{-1} and 390.8 kJ mol^{-1}, respectively, from selected literature data shown in Table 4.

The mean bond energies $\bar{E}$(Zn–C) and $\bar{E}$(M–N) [$\equiv \bar{E}$(M–R)] shown in Table 1 were obtained from eqs. e and f by using data from Tables 1 and 4.

Conclusions

From the mean bond energies $\bar{E}$(M–X) listed in Table 1, the following conclusions emerge, (a) the trend in $\bar{E}$(M–N) values is $Zn \gg Cd \gg Hg$; (b) $\bar{E}(Zn\text{–}CH_2SiMe_3) \gg \bar{E}(Zn\text{–}CH_2CMe_3)$; and (c) $\bar{E}(Zn\text{–}N) > \bar{E}(Zn\text{–}CH_2SiMe_3) > \bar{E}(Zn\text{–}CH_2CMe_3)$. With regard to (a), it is evident that the group 12 sequence (d^{10} complexes) mirrors that proposed for main group metal sub-groups, and is the reverse of that for a transition metal series; it is in line with trends in ΔH_v for the metal M (M = Zn, Cd, or Hg). Turning to (b), we had earlier suggested that the weakness of the M–CH_2CMe_3 bond in Ti^{IV}, Zr^{IV}, or Hf^{IV} alkyls was attributable to a steric effect [5]. We find it surprising that, even in the linear ZnR_2, a significant steric strain should contribute to weaken the Zn–CH_2CMe_3 bond relative to Zn–CH_2SiMe_3. It would be interesting to have accurate bond length data for these zinc alkyls ZnR_2 (R = CH_2CMe_3 or CH_2SiMe_3) in order to establish whether the thermochemical difference between these Zn–C bonds is reflected in geometrical data.

Experimental

Calorimetry

Enthalpies of hydrolysis and solution were measured using a calorimeter of 30

Table 5
Data relating to the heat of hydrolysis of $Zn[N(SiMe_3)_2]_2$ in 1 *M* aqueous HCl [a]

Experiment	Weight of sample (g)	R_i [b] (ohm)	R_f [b] (ohm)	ΔH_{obs} (kJ mol^{-1})
1	0.1229	1663.0	1619.5	518.1
2	0.1042	1662.0	1624.7	522.5
3	0.1178	1661.8	1619.7	522.8
4	0.0861	1661.0	1631.1	507.2
5	0.1203	1656.0	1613.2	522.8
6	0.1154	1659.0	1618.4	515.4
7	0.1353	1663.0	1614.7	523.3
8	0.1378	1661.9	1612.3	528.5
9	0.1410	1662.0	1611.8	521.8

[a] E_a (the energy equivalent of the calorimeter + contents) = 14.34 ± 0.93 kJ mol^{-1}; mean ΔH_{obs} = 520.3 ± 4 kJ mol^{-1}. [b] R_i and R_f are the initial and final resistances of the thermistor.

cm^3 capacity made of nylon suspended in a cylindrical brass can of radius 4.5 cm, similar in design to one described earlier [10] but approximately 1/10th the capacity; further details are in ref. 11. The air-space between the two vessels was filled with expanded polystyrene to reduce heat loss. The calorimetric fluid (either 1 *M* hydrochloric acid or 0.5 *M* sulphuric acid) was stirred by a stainless steel stirrer equipped with a device for breaking either one or two glass ampoules (containing a weighed amount of sample) held in nylon clips attached to the lid of the calorimeter. Temperature changes were detected by a thermistor inserted into the lid of the calorimeter, resistance changes being measured by a conventional Wheatstone bridge circuit and galvanometer system. The calorimeter in its jacket was placed in a water bath thermostat at 25 ± 0.1° C.

The calorimeter was calibrated electrically using an 8 watt heater attached to its lid, the heating period being adjusted to give a resistance-time profile similar to that produced by the hydrolysis reactions. A potentiometer was used to measure the current and voltage across the heater, the accuracy of measurement of power input

Table 6
Data relating to the heat of hydrolysis of $Hg[N(SiMe_3)_2]_2$ in 1 *M* aqueous H_2SO_4 [a]

Experiment	Weight of sample (g)	R_i [b] (ohm)	R_f [b] (ohm)	ΔH_{obs} (kJ mol^{-1})
1	0.1673	1661.0	1632.4	346.1
2	0.2005	1663.0	1629.0	342.8
3	0.1410	1661.1	1637.2	341.0
4	0.2111	1662.0	1626.8	337.4
5	0.2800	1662.0	1615.8	334.8
6	0.2098	1662.0	1627.0	337.5
7	0.2057	1662.0	1627.9	334.8
8	0.2564	1661.0	1619.3	329.8
9	0.2367	1661.0	1622.3	331.3

[a] E_a (the energy equivalent of the calorimeter + contents) = 14.71 ± 0.08 kJ ohm^{-1}; mean ΔH_{obs} = − 337.3 ± 4 kJ mol^{-1}. [b] R_i and R_f are the initial and final resistances of the thermistor.

Table 7
Boiling points of ZnR_2 ($R = CH_2CMe_3$ or CH_2SiMe_3) and $M[N(SiMe_3)_2]_2$ under reduced pressure and extrapolations to 760 Torr

Compound	Observed b.p. (° C/Torr)	Extrapolated b.p. (° C/760 Torr)
$Zn[CH_2CMe_3]_2$	58–59/9.7	180
$Zn[CH_2SiMe_3]_2$	44/1.5	195
$Zn[N(SiMe_3)_2]_2$	82/0.5	275
$Cd[N(SiMe_3)_2]_2$	93/0.5	288
$Hg[N(SiMe_3)_2]_2$	78/0.15	295

being better than 0.07%. The performance of the calorimeter was checked by measuring the enthalpy of neutralisation of tris(hydroxymethyl)methylamine by 0.1 *M* hydrochloric acid. The average of four determinations was 29.7 ± 0.3 kJ mol^{-1} (uncertainty equal to twice the standard deviation of the mean), in good agreement with the literature value of 29.77 ± 0.24 kJ mol^{-1} [12].

Compounds for hydrolysis were contained under dinitrogen in sealed ampoules of ca. 1 cm^3 capacity. Typical data sets for heats of hydrolysis are illustrated in Tables 5 and 6. The weight of compound used in each case was approximately 0.15 g, the resistance change during hydrolysis being ca. 30 ohm, corresponding to a temperature rise of ca. 0.4–0.5 ° C.

Group 12 metal alkyls and amides

The compounds ZnR_2 ($R = CH_2EMe_3$, $E = C$ or Si) [13] and $M[N(SiMe_3)_2]_2$ ($M = Zn$, Cd, or Hg) [14] were prepared by published procedures from the appropriate metal(II) chloride, $CdBr_2$, or HgI_2 and two equivalents of Mg(Cl)R or $Na[N(SiMe_3)_2]$. They were purified by fractional distillation (boiling points in Table 7), and their purity was checked by elemental analyses, IR and NMR spectroscopy.

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