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THERMODYNAMICS OF METAL—LIGAND BOND FORMATION

XXXII *. LEWIS ACIDITY OF PHENYL-ZINC AND -CADMIUM COMPOUNDS

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Summary

Thermodynamic data have been obtained by calorimetric titration in toluene at 30°C for the formation of adducts of Ph_2Cd and Ph_2Zn with heterocyclic bases. Cd readily becomes 4-coordinate, forming very stable 1/1 adducts with *o*-phen, bipy or tmed and both 1/1 and 2/1 adducts with 4-methylpyridine. Zn prefers to become 3-coordinate, forming very stable adducts $(Ph_2Zn)_2B$ with phen, bipy or tmed; only phen forms a 1/1 adduct and its enthalpy of formation is little greater. With 4-methylpyridine a stable 1/1 adduct is formed, but addition of further base is incomplete even with a large excess of base.

Introduction

While organomercury compounds of the type R_2Hg give no evidence of Lewis acidity unless the R group is highly electronegative, as in $(CF_3)_2Hg$ [1] or $(C_6F_5)_2Hg$ [2], organozinc and organocadmium compounds react readily with Lewis bases to form adducts in which the metal atom has a coordination number of three or four. Zinc compounds of this type which have been isolated include adducts R_2ZnB with ethers [3] and amines [4]; adducts with heterocyclic bases include those with bidentate bases such as 2,2′-bipyridine, which are brightly coloured [5]. Corresponding cadmium compounds are less stable [6], though Me_2Cd forms stable 1/1 adducts with chelating diethers and diamines [7].

Stability constants have been determined by oscillometry in benzene solution for adducts of Me_2Zn, Et_2Zn and i-Pr_2Zn with bipyridine, 1,2-diamino-

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ethane and *N,N,N′,N′*-tetramethyl-1,2-diaminoethane (tmed) [8] and some data have also been obtained for formation of the much less stable adducts of Me_2Zn with NEt_3, OEt_2 and SEt_2 [9]. Studies of the shifts of infrared spectra in solutions of Et_2Zn and Et_2Cd in various donor solvents show that the cadmium atom is "softer" than the zinc [10].

There appear to be no thermodynamic data reported for adduct formation by aryl-zinc and -cadmium compounds, but data have been reported for the mercury compound $(C_6F_5)_2Hg$ [11,12] and also for $(Cl_3C)_2Hg$ [13] and for the cyanide, $Hg(CN)_2$ [14]. We report here thermodynamic data, obtained by calorimetric titration in toluene solution at 30°C, for the reaction of Ph_2Zn and Ph_2Cd with the heterocyclic bases: 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), *N,N,N′,N′*-tetramethyl-1,2-diaminoethane (tmed) and 4-methylpyridine (mepy).

Experimental

Difficulty was experienced in getting solutions of organozinc and organocadmium compounds of adequate purity at the low concentrations used in calorimetric titration (10^{-3}—10^{-2} *M*). Preliminary experiments with ethylzinc gave solutions which reacted only slowly with heterocyclic bases because of the presence of polymeric oxidation products. Satisfactory results were obtained with phenyl, but even then it was necessary to handle all solutions under nitrogen specially freed from oxygen and water by passing over heated copper and then through concentrated sulphuric acid and over solid potassium hydroxide. For quantitative work solutions were prepared of approximately the required concentration and the exact concentration determined by analysis after completion of the calorimetric titration.

Diphenylcadmium was prepared by treatment of cadmium bromide with phenyllithium in ether under nitrogen [15]. After evaporation of the solvent the product was extracted with hot benzene, from which it was allowed to crystallise after filtration under nitrogen. Solutions of Ph_2Cd were prepared by dissolving the solid in toluene under nitrogen and were analysed after titration by the following method:

The solution, 2.0 ml, was evaporated to dryness and the residue digested with 8—10 drops of a mixture of concentrated sulphuric, nitric and perchloric acids (3/3/1) for 15 minutes. The volume was made up to about 50 ml with water and 10.0 ml of 5×10^{-3} *M* edta * added; the pH was then adjusted to 10 by addition of 15 *M* ammonia and excess edta titrated with 5×10^{-3} *M* magnesium sulphate, using eriochrome balck-T as indicator.

Diphenyl was prepared by reaction of zinc chloride and phenyllithium in ether under nitrogen [16]. After evaporation of the solvent the residue was dissolved in toluene, the solution filtered under pressure of nitrogen and made up to suitable volume. After completion of the calorimetric titration the zinc concentration was determined using edta, according to a method developed for mercury analysis [17].

Ether for use as solvent was dried over sodium and then distilled from sodi-

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edta = ethylenediaminetetraacetic acid.

um wire. Toluene was dried azeotropically by discarding the first 20% of distillate; the remainder was heated under reflux with molten sodium for 2 h before distillation and then used immediately. The liquid bases, mepy and tmed, were shaken with solid potassium hydroxide, then heated under reflux with calcium hydride before distillation. Bipy and phenanthroline hemihydrate were crystallised from ethanol and dried over silica gel in vacuo; solutions of phenanthroline were dried by azeotropic distillation before making up to volume.

Calorimetric titration was carried out on a LKB 8700 calorimeter, the calorimeter assembly being flushed with dry nitrogen and filled under nitrogen equilibration. The titration technique has been described previously [18]. Briefly, a solution of base in dry toluene was added incrementally to the toluene solution of the phenyl-zinc or -cadmium and the heat change observed after each addition; blank titrations were made to determine the heat of dilution of the base solution. Enthalpograms were obtained by plotting the total base concentration against the integrated, corrected heat change. All measurements were made at 30°C, the heat produced giving an overall temperature rise of less than 0.1°C.

Results and discussion

In most of these reactions the adduct stability is too high for the formation constant to be accurately evaluated by the calorimetric titration technique. Enthalpies of adduct formation given below are the average of at least three determinations and uncertainties are mean deviations. With 4-methylpyridine as base the titration curves obtained required the assumption that two adducts, $Ph_2M(mepy)$ and $Ph_2M(mepy)_2$, were obtained simultaneously. The method of calculation of the four parameters K_1, K_2, ΔH_1° and ΔH_2° from these results has been described [19].

Since the results obtained for reactions with bases are quite different for Ph_2Cd and Ph_2Zn, it is convenient to discuss the two compounds separately.

Diphenylcadmium. Enthalpograms for the reaction of Ph_2Cd with phen, bipy and tmed are shown in Fig. 1. With phen and tmed the reactions are virtually quantitative, 1/1 adducts being formed with the following enthalpy changes:

$$Ph_2Cd + phen \rightleftharpoons Ph_2Cd(phen) \qquad \Delta H^0 = -49 \pm 1 \text{ kJ mol}^{-1}$$

$$Ph_2Cd + tmed \rightleftharpoons Ph_2Cd(tmed) \qquad \Delta H^0 = -68 \pm 2 \text{ kJ mol}^{-1}$$

With bipy the adduct was less stable and the data show the formation of a 1/1 adduct with formation constant, $K \sim 1500$ l mol^{-1}:

$$Ph_2Cd + bipy \rightleftharpoons Ph_2Cd(bipy) \qquad \Delta H^0 = -35 \pm 2 \text{ kJ mol}^{-1}$$

For the titrations with 4-methylpyridine excellent fits of the experimental points to computed titration curves were obtained taking the following parameters for simultaneous formation of 1/1 and 2/1 adducts (K in l mol^{-1}, ΔH° in kJ mol^{-1}):

$$Ph_2Cd + mepy \rightleftharpoons Ph_2Cd(mepy) \qquad K_1 = 200,\ \Delta H_1^0 = -28$$

$$Ph_2Cd(mepy) + mepy \rightleftharpoons Ph_2Cd(mepy)_2 \qquad K_2 = 10,\ \Delta H_2^0 = -28$$

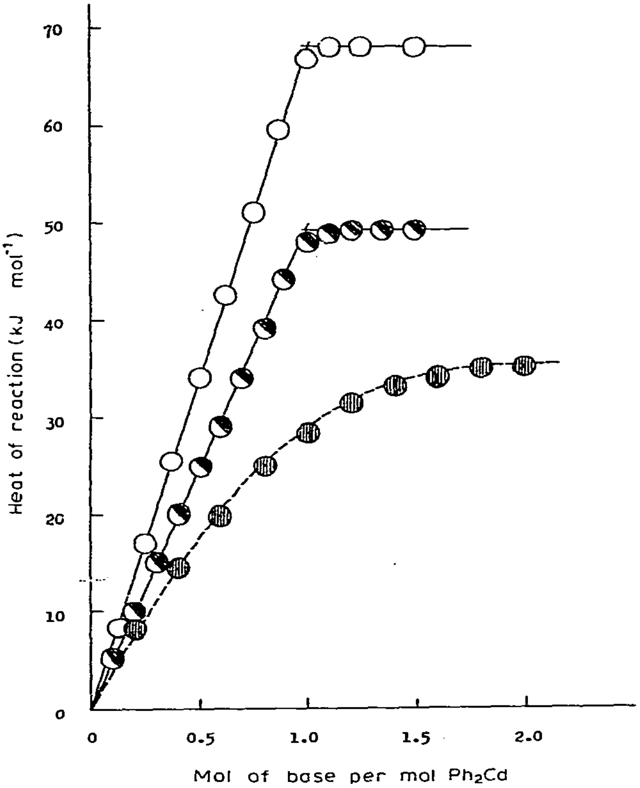

Fig. 1. Calorimeter titration of 10^{-2} *M* Ph_2Cd with tmed (open circles), phen (half shaded) and bipy (shaded circles).

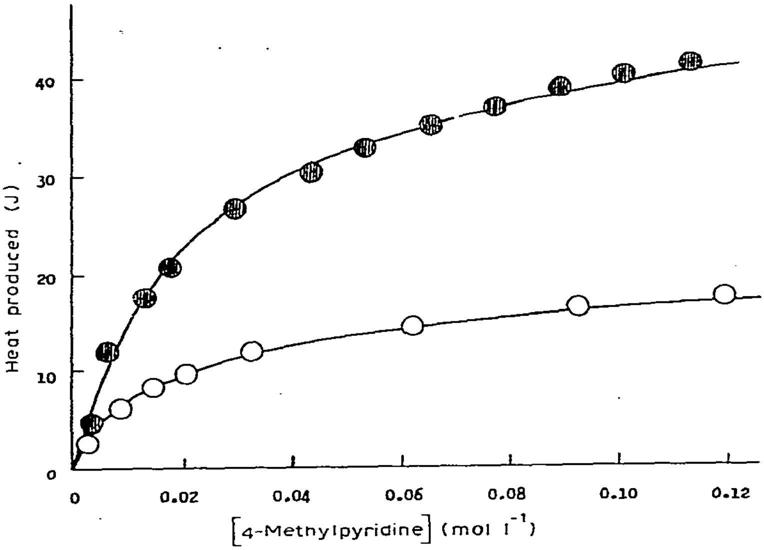

Fig. 2. Experimental points for calorimetric titration of 4-methylpyridine into Ph_2Cd, 4.0×10^{-3} *M* (open circles) and 9.9×10^{-3} *M* (shaded). Curves computed for $K_1 = 200$, $K_2 = 10$ l mol^{-1}, $\Delta H_1 = \Delta H_2 = -28$ kJ mol^{-1}.

with uncertainties of about ±30% in K_1 and K_2 and ±4 kJ mol^{-1} in ΔH_1° and ΔH_{1+2}°. The fit of experimental points to computed curves is shown in Fig. 2.

The enthalpy of formation of $Ph_2Cd(mepy)_2$ is between that of the 1/1 adducts with phen and tmed, showing that the Cd atom readily becomes 4-coordinate and the latter bases are chelate. The enthalpy of formation of the phen adduct and its stability are comparable to those of mercury compounds:

	Ph_2Cd	$Hg(C_6F_5)_2$[12]	$Hg(CCl_3)_2$[13]
$-\Delta H^0$	49	47	42
K	$>10^4$	2×10^3	$>10^4$

but these mercury compounds react with only one equivalent of 4-methylpyridine and other evidence suggests that the second Hg—N bond is much weaker than the first. In the case of Ph_2Cd these are about equal and the 1/1 adduct with 4-methylpyridine is much more stable than corresponding mercury compounds.

Diphenylzinc. Like Ph_2Cd, Ph_2Zn reacts with 4-methylpyridine in two steps, but the relationship between the steps is quite different. The 1/1 adduct first formed is more stable than that of Ph_2Cd with a larger enthalpy of formation:

$$Ph_2Zn + mepy \rightleftharpoons Ph_2Zn(mepy) \qquad K_1 \sim 10^3,\ \Delta H_1^0 = -47 \pm 5$$

Further reaction with base does not go to completion, even with a large excess (Fig. 3); indeed it is possible that the continuing production of heat when excess base is added arises from some other reaction. If it is assumed that it is

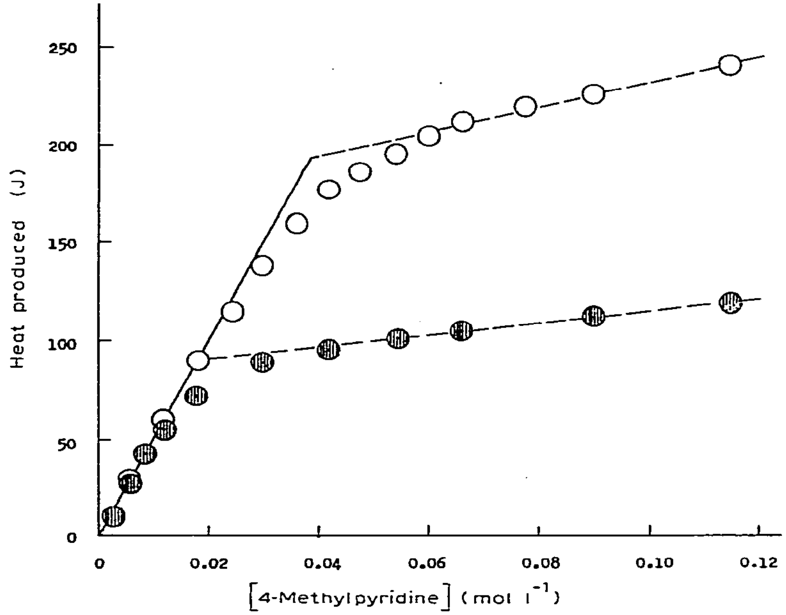

Fig. 3. Experimental points for calorimetric titration of 4-methylpyridine into Ph_2Zn, 3.8×10^{-2} *M* (open circles) and 1.9×10^{-2} *M* (shaded). Lines drawn for quantitative formation of $Ph_2Zn(mepy)$ and incomplete formation of $Ph_2Zn(mepy)_2$.

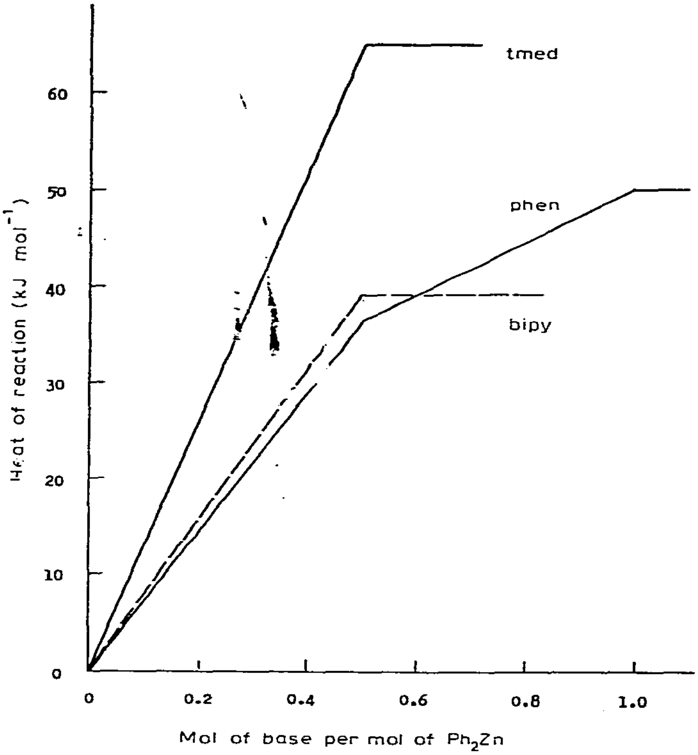

Fig. 4. Calorimetric titration of 1.0—4.0 X 10^{-2} *M* Ph_2Zn with bidentate bases in toluene solution at 30°C.

due to the formation of $Ph_2Zn(mepy)_2$ and that $\Delta H_1^\circ = \Delta H_2^\circ$ then $K_2 << 10$. The zinc atom is thus clearly reluctant to increase its coordination number beyond three.

The reactions with bidentate bases are remarkable. Enthalpograms are shown in Fig. 4 for reaction with phen, bipy and tmed. When Ph_2Zn reacts with phen reaction ceases after formation of a 1/1 adduct, but there is a sharp change in the slope of the enthalpogram corresponding to the formation of a highly stable adduct $(Ph_2Zn)_2$phen. With the other two bases this is the only stoichiometry observed, enthalpies of adduct formation being as follows:

Ph_2Zn + phen $\rightleftharpoons$ Ph_2Zn(phen) $\Delta H^0 = -50 \pm 3$ kJ mol^{-1}

2 Ph_2Zn + phen $\rightleftharpoons$ $(Ph_2Zn)_2$phen $\Delta H^0 = -37 \pm 1$ kJ(g-at.Zn)$^{-1}$

2 Ph_2Zn + bipy $\rightleftharpoons$ $(Ph_2Zn)_2$bipy $\Delta H^0 = -39 \pm 1$ kJ(g-at.Zn)$^{-1}$

2 Ph_2Zn + tmed $\rightleftharpoons$ $(Ph_2Zn)_2$tmed $\Delta H^0 = -65 \pm 5$ kJ(g-at.Zn)$^{-1}$

In most of these adducts the two N atoms are clearly independent, each being coordinated to a different zinc atom, which becomes 3-coordinate. Surprisingly there is no evidence for bipy or tmed behaving as chelates and the reluctance of the zinc atom to become 4-coordinate is shown by the data for phen, the structure of which particularly favours chelation: even in this case when chelation occurs the enthalpy change associated with formation of the second Zn—N bond is only third of the first. Though chelate 1/1 adducts with bipy or tmed may be formed in the solid state or in concentrated solution, it is evident that in dilute solutions these bases give only 3-coordinate adducts.

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