Thermochemical Behaviour of some Tetrahedral Dihalogenodi(tertiary phosphine)cobalt(II) Complexes

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The thermochemical behaviour of a series of complexes of the type [L_2CoX_2] (L = PR_3 where R = Me, Et, Pr^i, Pr^n, Bu^n, Ph, or C_6H_{11}; X = Cl, Br, or I) has been studied. Heats of decomposition have been measured and the variation in the values obtained is discussed in terms of the factors which influence the stability of the complexes, in particular the cobalt–phosphorus bond strength.

TRANSITION-METAL complexes containing organophosphorus ligands have been extensively studied;[1,2] however, the role of the vacant phosphorus 3*d* orbitals in determining the nature of the phosphorus–metal bond is still controversial.[3,4] Although the phosphorus–metal

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[1] C. A. McAuliffe, 'Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands,' Macmillan, London, 1973.

[2] G. Booth, 'Organic Phosphorus Compounds,' Interscience, New York, 1973, vol. 1, ch. 3.

[3] J. G. Verkade, *Co-ordination Chem. Rev.*, 1972, **9**, 1.

[4] L. D. Pettit, *Quart. Rev.*, 1971, **25**, 1.

bond has been studied by a variety of techniques, there is only a relatively small amount of thermochemical data available that directly concerns the P–M bond.[5]

Recently, it has been shown that complexes of the type $[L_2CoCl_2]$ ($L = PPh_2Bu$, $PPhBu_2$, or PBu_3), when heated in an inert atmosphere, thermally decompose by loss of the phosphorus-containing ligand.[6] We have extended this study to include a large range of ligands. More importantly, using the technique of differential thermal analysis (d.t.a.) it has been possible to measure the variation in phosphorus–metal bond strength as the substituents on the phosphorus atom are varied. Bonding arguments based on the heats of solid-state decompositions involve assumptions concerning the variation in lattice forces with changes in the ligand and variations of the central metal ion in the complex. Generally it is assumed that small changes in the ligand, or replacement of the central metal atom with one of similar size and charge, do not seriously alter the molecular-lattice forces.[7–9] Justification for this is usually based on the similar enthalpy of solution for the complexes. The validity and application of this approach is of some concern.[10,11] Furthermore, the enthalpy of sublimation has been measured for a series of related complexes and, although the data are limited, in some cases the enthalpies vary only slightly with minor changes in the ligand [12] whereas for others the variation is considerable.[13] The complexes used in the present study are particularly suited to a d.t.a. investigation of the variation in phosphorus–metal strength, since they all melt before decomposition, thus eliminating lattice forces in the treatment of the data. This, however, necessitates assumptions concerning the significance of the heat of vaporization of the complex in the observed heat of decomposition. Arguments are presented as to the treatment of these assumptions.

EXPERIMENTAL

The phosphine ligands were purchased from Maybridge Chemical Co., Tintagel, and used without further purification. The anhydrous cobalt salts were prepared by heating under vacuum the commercially available hydrated salt to 100 °C for 2 h. The preparation of the complexes followed the literature methods.[14] The phosphine was introduced into an Erlenmeyer flask containing absolute ethanol (*ca.* 20 cm^3) and the flask was then swept with nitrogen. The cobalt salt (0·5 mol equiv.) was dissolved in absolute ethanol (*ca.* 20 cm^3) and added to the phosphine solution. The system was then warmed to 50 °C for 2 h under a nitrogen atmosphere. The complexes generally crystallized on cooling the solution and were recrystallized from dichloromethane–pentane mixtures. All complexes were identified by C and H analysis and m.p. The following complexes are previously unreported: $[(Pr^i{}_3P)_2CoCl_2]$ (Found: C, 46·4; H, 9·55. Calc.: C, 46·4; H, 9·55%), m.p. 117—120 °C; $[(Ph_2MeP)_2CoBr_2]$ (Found: C, 49·8; H, 4·30. Calc.: C, 50·45; H, 4·25%), m.p. 152 °C; and $[(Ph_2MeP)_2CoCl_2]$ (Found: C, 59·1; H, 5·15. Calc.: C, 58·9; H, 4·95%), m.p. 163 °C. The complex $[(Pr^i{}_3P)_2CoCl_2]$ slowly loses $PPr^i{}_3$ at room temperature, but can be stored for several months at −10 °C. M.p.s were determined on a Gallenkamp apparatus. Microanalyses were by Miss G. Reilly of this department. I.r. data were recorded on a Perkin-Elmer model 451 spectrometer, calibrated with the 381·4 cm^{-1} peak of indene. The spectra were obtained as Nujol mulls between polyethylene plates.

Thermogravimetric data were obtained with a Stanton Redcroft TG-750 thermobalance at heating rates of 10 and 20 °C min^{-1} in a dynamic nitrogen atmosphere. Generally 3—5 mg sample weights were used. The differential thermal analysis (d.t.a.) data were obtained with a Stanton Standata 6-25 apparatus at a heating rate of 20 °C min^{-1} in a dynamic N_2 atmosphere. Sample weights of 5—10 mg of the pure complex were generally used, with alumina (5·0 mg) as reference material. The instrument was calibrated with the heat of fusion of both Sn and Pb (99·999%, Koch–Light). The values reported are an average of at least three determinations and are accurate to ±4%. Peak areas were measured with a planimeter.

RESULTS AND DISCUSSION

Magnetic and spectroscopic measurements [1] have shown that the complexes under consideration have tetrahedral geometry (C_{2v} symmetry), thus two metal–halide stretching frequencies are expected. The two strong bands observed in the metal–chlorine stretching region (Table 1) confirm the tetrahedral geometry of all complexes studied. Weak to medium bands, at *ca.* 275 cm^{-1}, were also seen in most complexes; however, such bands can be attributed to ligand vibrations.[15] The cobalt–chlorine frequency appears to be dependent on the nature of the phosphine ligand, increasing as the number of phenyl substituents on the phosphorus atom increases. Similar variation in metal–chlorine stretching frequency has been noted previously in many square-planar platinum(II)–phosphine complexes.[16]

TABLE 1

Cobalt–chlorine stretching wavenumbers (cm^{-1})

Complex	Wavenumber	
$[\{(C_6H_{11})_3P\}_2CoCl_2]$	315s	305s
$[(Pr^i{}_3P)_2CoCl_2]$	319s	300s
$[(Bu^n{}_3P)_2CoCl_2]$	330s	295m
$[(Et_3P)_2CoCl_2]$	330s	295m
$[(Pr^n{}_2PhP)_2CoCl_2]$	332s	300s
$[(PhEt_2P)_2CoCl_2]$	335s	300s
$[(Ph_2EtP)_2CoCl_2]$	335s	310s
$[(Ph_3P)_2CoCl_2]$	344s	310s

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[6] K. Moedritzer and R. F. Miller, *J. Therm. Anal.*, 1969, **1**, 151.

[7] G. Beech, C. T. Mortimer, and E. G. Tyler, *J. Chem. Soc.* (*A*), 1969, 1111.

[8] G. Beech, C. T. Mortimer, and E. G. Tyler, *J. Chem. Soc.* (*A*), 1967, 925.

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[11] F. R. Hartley, *Chem. Rev.*, 1973, **73**, 163.

[12] C. T. Mortimer and J. L. McNaughton, *Thermochim. Acta*, 1974, **8**, 265.

[13] C. T. Mortimer and J. L. McNaughton, *Thermochim. Acta*, 1974, **10**, 125.

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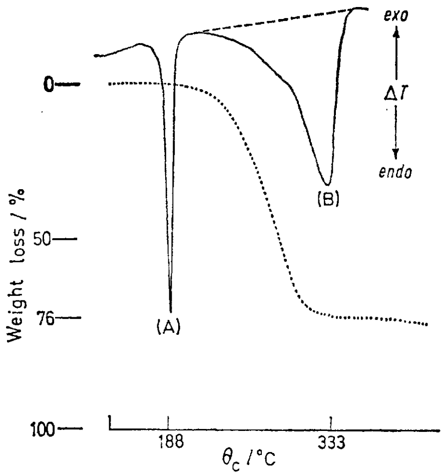
[15] E. A. Allen and W. Wilkinson, *Spectrochim. Acta*, 1974, **A30**, 1219.

[16] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Co-ordination Chem. Rev.*, 1973, **10**, 335.

The thermogravimetric data are given in Table 2 and the curve for $[(Ph_2EtP)_2CoCl_2]$ is shown in the Figure. The data indicate that complexes of the type $[L_2CoX_2]$ (L = phosphine ligand and X = Cl or Br) decompose simply by complete loss of the phosphine ligand, which is given off as a gas, leaving the cobalt dihalide residue which on continued heating decomposes to cobalt metal.



D.t.a. (——) and t.g.a. (· · · ·) curves for $[(Ph_2EtP)_2CoCl_2]$

TABLE 2

Thermogravimetric data

Complex	CoX_2 Residue (%) Calc.	CoX_2 Residue (%) Found	Co Residue (%) Calc.	Co Residue (%) Found	Decomposition temperature (θ_c/°C)
$[(Ph_3P)_2CoCl_2]$	19·8	21·5	9·0	10·5	160
$[(Ph_2EtP)_2CoCl_2]$	23·3	22·8	10·6	11·0	170
$[(Ph_2MeP)_2CoCl_2]$	24·5	25·9	11·1	10·5	158
$[(Pr^n{}_2PhP)_2CoCl_2]$	25·1	26·9	11·4	12·6	127
$[(PhEt_2P)_2CoCl_2]$	28·1	28·0	12·8	13·5	80
$[(Et_3P)_2CoCl_2]$	35·5	36·5	16·1	16·5	80
$[(Bu^n{}_3P)_2CoCl_2]$	24·3	25·5	11·0	12·2	107
$[(Pr^i{}_3P)_2CoCl_2]$	28·8	28·4			107
$[\{(C_6H_{11})_3P\}_2CoCl_2]$	18·8	16·5			94
$[(Ph_3P)_2CoBr_2]$	29·4	29·8	7·9	7·4	193
$[(Ph_2EtP)_2CoBr_2]$	33·8	34·0	9·1	8·5	158
$[(Ph_2MeP)_2CoBr_2]$	35·3	35·5	9·5	9·5	158
$[(PhEt_2P)_2CoBr_2]$	39·7	39·4	10·7	9·0	120
$[(Et_3P)_2CoBr_2]$	48·2	46·7			120

For all the solid complexes examined, melting preceded decomposition. The mode of decomposition, however, was found to depend on the sample weight used. This is a recognized phenomena in thermoanalytical studies[17] and has been thoroughly discussed in terms of the atmosphere produced in the immediate area of the sample.[18,19] As the sample weight increased, the mode of decomposition approached a two-step process [reactions (1) and (2)].

$$[L_2CoX_2](l) \longrightarrow [LCoX_2](l) + L(g) \qquad (1)$$

$$[LCoX_2](l) \longrightarrow CoX_2(s) + L(g) \qquad (2)$$

We were unable to separate the two steps. Complexes of the type $[LCoX_2]$ are known where L = a secondary phosphine[20] or arsine.[21] Also complexes where L = a nitrogen-containing ligand are known to decompose in a two-step process.[11] With small sample weights (5—10 mg) the decomposition proceeded by the overall reaction (3), with no indication of intermediate $[LCoX_2]$. It is

$$[L_2CoX_2](l) \longrightarrow CoX_2(s) + 2L(g) \qquad (3)$$

important to note that consistent data for the enthalpy of decomposition could only be obtained when the decompositions occurred by reaction (3). We also examined a number of similar iodide complexes; however, the thermal gravimetric analysis (t.g.a.) data indicated these decompose in a complicated manner.

The d.t.a. data are given in Table 3 and the thermogram for $[(Ph_2EtP)_2CoCl_2]$ is illustrated in the Figure. Peak (A) is characteristic of a m.p. peak obtained by the d.t.a. method and correlates well with the reported m.p. of the complex. Peak (B), correlated with the t.g.a. data, is identified as the thermal effect due to loss of the phosphine ligands. The area under this peak is related to the heat of decomposition of the complex, reaction (3). The reported values are not corrected to a common temperature; however, it is unlikely that this correction will alter the sequence of the heats of decomposition. Peak maxima are also listed in Table 3. It should be noted that these are a function of the conditions of the d.t.a. experiment and not characteristic of the complex. The decomposition peak for the complex $[(Ph_3P)_2CoCl_2]$ could not be separated from the m.p. peak. However, by comparison with the bromides, the sequence of ΔH values is most likely $PPh_3 > PPh_2Et$. The complex $[\{(C_6H_{11})_3P\}_2CoCl_2]$ gave an anomalously large enthalpy of decomposition. Under the conditions of the d.t.a. experiment the ligand also decomposed.

The relative σ-donor strength of phosphine ligands can be determined by basicity measurements. The available pK_a values[22] are listed in Table 3. The pK_a of the $PPr^i{}_3$ ligand is unreported, but is expected to be less than that of the straight-chain isomer.[22] The data in Table 3 show the heat of decomposition to increase as the σ-donor ability of the phosphine ligand decreases. The $PPr^i{}_3$ and $PBu^n{}_3$ ligands are slightly anomalous, but this is undoubtedly due to steric effects.[23] It is of interest to note that this sequence of heats of decomposition is similar to that of the platinum–phosphorus coupling constant in a series of square-planar Pt^{II} complexes.[24]

The thermal stability of a solid, *i.e.* the temperature at the beginning of loss of weight, does not represent an established physical parameter[16,21] and bonding arguments based on data of this type are of questionable validity. The complexes we have studied all melt before

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[17] W. W. Wendlandt and J. P. Smith, ' The Thermal Properties of Transition Metal Ammine Complexes,' Elsevier, Amsterdam, 1969, p. 2.

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[19] A. Blazek, ' Thermal Analysis,' Van Nostrand, London, 1973, p. 110.

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[24] S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, 1967, **6**, 1133.

decomposition thus eliminating lattice forces and in view of the similarity of the ligands are most likely to decompose by the same mechanism. Under these conditions, the decomposition temperatures may well reflect bond strengths. The decomposition temperatures reported in Table 2 are in general agreement with the d.t.a. data obtained. The thermal stability of the series $[CoCl_2(PBu_nPh_{n-3})]_2 (n = 1—3)$ was also found[6] to decrease as n increases. Again these complexes melt before decomposition and are likely to decompose by the same mechanism.

Ideally, bonding arguments should be based on the heat of gas-phase reactions. The observed heat of decomposition, $\Delta H(3)$, is related to the heat of decomposition in the gas phase, $\Delta H(g)$, by the following thermodynamic cycle and $\Delta H(3) = \Delta H(g) - \Delta H(sub) + \Delta H(v)$, where $\Delta H(v)$ is the heat of vaporization of the

$$\begin{tikzcd}
{[L_2CoX_2](g)} \arrow[r, "\Delta H(g)"] & CoX_2(g) + 2L(g) \\
{[L_2CoX_2](l)} \arrow[u, "\Delta H(v)"] \arrow[r, "\Delta H(3)"] & CoX_2(s) + 2L(g) \arrow[u, "\Delta H(sub)"']
\end{tikzcd}$$

complex and $\Delta H(sub)$ the heat of sublimation of the cobalt halide. When comparing $\Delta H(g)$ for complexes with different phosphine ligands in a constant metal-halide series the term $\Delta[\Delta H(sub)]$ is zero and equation (4)

$$\Delta[\Delta H(3)] = \Delta[\Delta H(g)] + \Delta[\Delta H(v)] \qquad (4)$$

is obtained. This assumes the cobalt dihalide formed in the decomposition always takes the same crystalline form. Since the d.t.a. curves show no further phase changes, this assumption is quite reasonable.

The term $\Delta[\Delta H(v)]$, the difference in the heat of vaporization of the complexes, is taken to be small compared to $\Delta[\Delta H(3)]$, thus $\Delta[\Delta H(g)] \approx \Delta[\Delta H(3)]$. Evidence for this is based on thermochemical data obtained for a series of planar Pt^{II} complexes of the type $[(R_3P)_2PtX_2]$. The heat of vaporization of these complexes is known to reflect that of the phosphine ligand in the complex.[25] In a constant-halide series, $\Delta[\Delta H(v)]$(complex), the difference in the heat of vaporization of the complexes, was found to be somewhat less than $\Delta[\Delta H(v)]$(ligand), the difference in the heat of vaporization of the phosphine ligands. Thus, if $\Delta[\Delta H(3)]$ reflected mainly the $\Delta[\Delta H(v)]$ term in equation (4), it would be expected to vary in a similar fashion as the heat of vaporization of the phosphine ligands. Table 3 lists the heat of vaporization for some ligands and shows that this is not the case.

TABLE 3

Enthalpies of the reaction $[L_2CoX_2](l) \longrightarrow CoX_2(s) + 2L(g)$

Complex	ΔH / kJ mol^{-1}	Peak (B) maxima (°C)	$\Delta(\Delta H)$ / kJ mol^{-1}	$\Delta H(v)$ [a] of phosphine ligand / kJ mol^{-1}	pK_a [a] of phosphine ligand
$[(Ph_3P)_2CoCl_2]$	>188	343	>125	71·1	2·73
$[(Ph_2EtP)_2CoCl_2]$	210	333	147	*ca.* 58·6 [b]	
$[(Ph_2MeP)_2CoCl_2]$	168	333	105	*ca.* 58·6 [b]	
$[(Pr^n{}_2PhP)_2CoCl_2]$	161	294	97		
$[(PhEt_2P)_2CoCl_2]$	140	294	77	52·1	6·25
$[(Et_3P)_2CoCl_2]$	129	283 (broad)	66	*ca.* 35·6 [b]	8·69
$[(Bu^n{}_3P)_2CoCl_2]$	97	283 (broad)	34	53·6	8·43
$[(Pr^i{}_3P)_2CoCl_2]$	63	225 (broad)	0		*ca.* 8·5
$[(Ph_3P)_2CoBr_2]$	157	381	118	71·1	2·73
$[(Ph_2EtP)_2CoBr_2]$	118	323	79	*ca,* 58·6 [b]	
$[(Ph_2MeP)_2CoBr_2]$	82	323	43	*ca.* 58·6 [b]	
$[(PhEt_2P)_2CoBr_2]$	71	294	32	52·1	6·25
$[(Et_3P)_2CoBr_2]$	39	270 (broad)	0	*ca.* 35·6 [b]	8·69

[a] From G. Booth, ' Organic Phosphorus Compounds,' Wiley–Interscience, New York, 1972, vol. 1. [b] Estimated using Trouton's rule.

Furthermore, by comparison with the platinum data, the expected variation in the enthalpy of vaporization of the complexes cannot account for the magnitude of the $\Delta[\Delta H(3)]$ term. The $\Delta[\Delta H(3)]$ values for the cobalt complexes in Table 3 are based on the least stable complex for each halide series.

The gas-phase enthalpy change may be split into a number of individual contributions and for different phosphine ligands in a given halide series expressed as in (5). The term $\Delta[\Delta H(hyb)](L)$ expresses the enthalpy

$$\Delta[\Delta H(3)] \approx \Delta[\Delta H(g)] = \Delta[\Delta H(hyb)](L) + \Delta[\Delta H(hyb)](CoX_2) + \Delta[\Delta H(c.f.s.e.)] + \Delta[\Delta H(Co\text{–}L)] \qquad (5)$$

difference due to rehybridization of the phosphine ligands on co-ordination. The interatomic C–P–C angles in the free ligands PMe_3 and PPh_3 are 99·1 and 102·99° respectively.[26,27] When complexed, the C–P–C angles for both ligands are expected to be close to the tetrahedral value. Thus this term is expected to be very small. Similarly, the term $\Delta[\Delta H(hyb)](CoX_2)$ expresses the enthalpy difference due to rehybridization of ' CoX_2 ' in the

[25] E. A. Allen, J. Del Gaudio, and W. Wilkinson, *Thermochim. Acta*, 1975, **11**, 197.

[26] D. R. Lide, jun., and D. E. Mann, *J. Chem. Phys.*, 1958, **29**, 914.

[27] R. L. Kuczkowski and D. R. Lide, *J. Chem. Phys.*, 1967, **46**, 357.

complexes to that in the product. Since the complexes are all of pseudotetrahedral symmetry and for a given halide series the CoX_2 product assumes the same crystalline structure, this term is expected to be very small. The term $\Delta[\Delta H(\text{c.f.s.e.})]$ expresses the change in crystal-field stabilization energy with change in phosphine ligand. The direction of this change is difficult to judge. In a series of *trans* square-planar d^8 complexes, electron-releasing substituents on the phosphorus atom decreased the ligand-field strength.[28] This trend has also been observed in a series of trigonal-bipyramidal Ni^{II} complexes.[29] However, for tetrahedral Ni^{II} complexes the opposite effect was observed.[28,30] In a series of Co^{II} complexes the ligands tricyclohexyl- and triphenylphosphine, although quite different in basicity, were found to have a similar effect on the ligand-field strength.[14] In view of the similarity of the ligands involved it is unlikely that variations in c.f.s.e. alone can account for the magnitude of $\Delta[\Delta H(3)]$. The term $\Delta[\Delta H(\text{Co–L})]$ expresses the difference in the enthalpy of interaction between the phosphine ligands and the cobalt metal centre, *i.e.* the difference in bond strength for different phosphine ligands, and is the major contribution to the observed $\Delta[\Delta H(3)]$. The observed increase in metal–phosphorus bond strength with decreasing basicity of the phosphine ligand can be interpreted in two ways. First, the π-bonding ability of the phosphorus ligand is expected to increase as the electron-withdrawing ability of the phosphorus substituents increases. Thus the π-bonding ability of the ligand will determine the nature of the bond. Alternatively, applying Bent's rule,[31] the electron-withdrawing substituents cause an increase in *s* character of the phosphorus lone-pair orbital, contracting the orbital, and providing a more stable σ donor, thus forming a stronger cobalt–phosphorus bond.

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