Microcalorimetric Studies on the Thermal Decomposition of Platinum and Palladium Complexes containing Phosphine or Diene Ligands

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Microcalorimetric measurements of the enthalpies of thermal decomposition of several complexes of Pt and Pd containing phosphine or diene ligands have been carried out, leading to the following values for the enthalpies of formation, $\Delta H_f^\ominus$(c)/kJ mol^{-1} of the crystalline compounds: *cis*-[Pt(PEt$_3$)$_2$Cl$_2$] = −(655 ± 15); *trans*-[Pt(PEt$_3$)$_2$Cl$_2$] = −(644 ± 7); *trans*-[Pt(PPr$^i_3$)$_2$Cl$_2$] = −(785 ± 7); *trans*-[Pt{P(C$_6$H$_{11}$)$_3$}$_2$Cl$_2$] = −(999 ± 8); *cis*-[Pd(PPh$_3$)$_2$Cl$_2$] = 205 ± 10; *cis*-[Pt(PPh$_3$)$_2$Cl$_2$] = 173 ± 6; *cis*-[Pt(PMe$_2$Ph)$_2$Cl$_2$] = −(280 ± 5); *cis*[Pd(cod)Cl$_2$] = −(234 ± 1)-(cod = cyclo-octa-1,5-diene); *cis*-[Pt(cod)Cl$_2$] = −(241 ± 9); *cis*-[Pt(PEt$_3$)$_2$Me$_2$] = −(520 ± 6); *cis*-[Pt(PEt$_3$)$_2$(C$_6$H$_4$Me-*o*)$_2$] = −(329 ± 24); *cis*-[Pt(PEt$_3$)$_2$(CH$_3$)Cl] = −(569 ± 5) *cis*-[Pt(PEt$_3$)$_2$(C$_6$H$_4$Me-*o*)Cl] = −(495 ± 15); *cis*-[Pt(PEt$_3$)$_2$(SEt)$_2$] = −(651 ± 9); *cis*-[Pt(PPh$_3$)$_2$(SEt)$_2$] = 182 ± 14; *cis*-[Pd(MeCN)$_2$Cl$_2$] = −(149 ± 3); [Pt(PEt$_3$)$_2$Cl$_4$] = −(863 ± 7). Enthalpies of sublimation of six of these compounds were measured by the vacuum-sublimation microcalorimetric technique, allowing estimates to be made for the remainder. The derived $\Delta H_f^\ominus$ for the gaseous complexes have served to derive bond-enthalpy contributions of L $\longrightarrow$ Pt and Pt–X bonds in [PtL$_2$X$_2$] compounds. The ligand bonding power to PtCl$_2$ decreases along the series PPr$^i_3$ > P(C$_6$H$_{11}$)$_3$ > PEt$_3$ > PPh$_3$ > olefin (in cyclo-octa-1,5-diene). Bond-enthalpy contributions of Pt–X [relative to $\bar{E}$(Pt–Cl) = 290 kJ mol^{-1}] decrease in the series Pt–C* ~ Pt–Cl > Pt–C > Pt–S, where C* and C are trigonal and tetrahedral carbon (in Ph–Pt and CH$_3$–Pt bonds, respectively).

Thermochemical data on complexes of platinum and of palladium with phosphine or olefin ligands are sparse, and virtually limited to those obtained by Mortimer, Ashcroft, and co-workers [1-4] on [Pt(PEt$_3$)$_2$Ph$_2$], [Pt(PPh$_3$)$_2$(COPh)Cl], [Pt(PPh$_3$)$_2$(C$_2$H$_4$)], and [{Pd(CH$_2$CH=CH$_2$)Cl}$_2$]. The present work reports on the application of the high-temperature microcalorimeter to thermal-decomposition studies [5] on selected Pt and Pd complexes with phosphines (PR$_3$) or cyclo-octa-1,5-diene (cod) as ligands. It was possible to sublime some of these complexes without decomposition from the hot zone of the microcalorimeter, to obtain enthalpies of formation, $\Delta H_f^\ominus$(g), of the gaseous complexes. These provide a basis for the evaluation of the bond-energy contributions of Pt–X and L $\longrightarrow$ Pt in [PtL$_2$X$_2$] molecules for various ligands, L, with X = Cl, CH$_3$, C$_6$H$_4$Me-*o*, or SEt.

Experimental

The microcalorimeter and its operation have been described previously.[5]

Compounds.—The platinum and palladium complexes were synthesised by established methods.[6-11] Samples were characterized by elemental analysis, melting/decomposition points, i.r. and ^{31}P n.m.r. spectra.

Auxiliary Data.—The following auxiliary $\Delta H_f^\ominus$ values (kJ mol^{-1}) were used in the evaluation of the present experimental results (certain of the chosen values are based on estimates): PtCl$_2$(c) = −(140.6 ± 4);[12] PdCl$_2$(c) = −(163.2 ± 8);[13] PMe$_3$(g) = −(101 ± 5);[14] PEt$_3$(g) ~ −108 [estimated value; a literature value,[14] $\Delta H_f^\ominus$(g) ~ −49.6 kJ mol^{-1}, leads to a seemingly low bond energy $\bar{D}$(P–Et), relative to $\bar{D}$(P–Me) and $\bar{D}$(P–Ph). From plots of $\bar{D}$(M–R) (M = N, P, As, Sb, or Bi; R = Me, Et, or Ph) given by Pilcher and Skinner[15] the estimated $\Delta H_f^\ominus$ ~ −108 kJ mol^{-1} is consistent with the general trend]; PPh$_3$(g) = 314 ± 14;[14] PPr$^i_3$(g) ~ −148 (estimated from application of the Allen scheme, *e.g.* ref. 16); P(C$_6$H$_{11}$)$_3$(g) ~ −205 (estimated from application of the Allen scheme); P(Me$_2$Ph)$_3$(g) ~ 37 [estimated from $\frac{2}{3}\Delta H_f^\ominus$(PMe$_3$) + $\frac{1}{3}\Delta H_f^\ominus$(PPh$_3$)]; PCl$_3$(g) = −(289.5 ± 1);[17] MeCl(g) = −(82.0 ± 0.5);[14] EtCl(g) = −(112.1 ± 0.5);[14] Pr^{i}Cl(g) = −(145 ± 0.6);[14] C$_6$H$_{11}$Cl(g) = −(163.6 ± 3.6);[14] PhCl(g) = 51.3 ± 0.7;[14] C$_6$H$_5$CH$_2$Cl(g) = 18.7 ± 3;[14] C$_2$H$_6$(g) = −(84.0 ± 0.2);[14] C$_{14}$H$_{14}$(g) = 143 ± 1.8;[14] cyclo-C$_8$H$_{12}$(g) = 58.6 ± 1.2;[14] cyclo-C$_8$H$_{12}$Cl$_2$(g) ~ −121 (estimated, assuming ΔH for addition of Cl$_2$ to cod is of similar magnitude to ΔH for addition to C$_2$H$_4$); SEt$_2$(g) = −(83.5 ± 0.8);[14] P(S)Et$_3$(g) ~ −218 (estimated [18]); P(S)Ph$_3$(g) ~ 204 (estimated [18]); MeCN(g) = 74.0 ± 0.4.[19]

Measured ΔH^T at elevated temperatures were converted to room-temperature values, ΔH^{298}, using ($H_T - H_{298}$) data tabulated by Stull *et al.*[20] and by Barin and Knacke.[21] Values of ($H_T - H_{298}$) for the phosphines are not available, and were estimated from data on the corresponding amines.

Results

cis-*Dichlorobis(triethylphosphine)platinum*(II), [Pt(PEt$_3$)$_2$Cl$_2$].—Thermal-decomposition (t.d.) studies were made over the range 470—603 K. At the highest temperatures, a platinum mirror formed in the reaction vessel, and a white powder settled in the cooler exit-tube. At temperatures below 550 K, there was no mirror formation and the main change appeared to be sublimation of the complex, with only slight decomposition. The vacuum-sublimation (v.s.) technique was satisfactorily applied at 470 K, and results providing ΔH_{sub} for the complex are included in Table 1.

The thermal decomposition at 603 K involves the primary step [equation (1)] accompanied by chlorination of liberated phosphine [equation (2)] and thermal rearrangements [*e.g.* equation (3)]. The white powder deposited in the exit-tube

Table 1. Sublimation and thermal decomposition of *cis*-$[Pt(PEt_3)_2Cl_2]$

Sample mass (mg)	Method	T/K	ΔH_{sub}^{T} / kJ mol^{-1}	ΔH_{sub}^{298} / kJ mol^{-1}
2.829	v.s.	470	266.7	185.3
2.019	v.s.	470	239.3	157.9
2.081	v.s.	551	305.0	177.3
				Mean 173.5 ± 16

Sample mass (mg)	Method	T/K	ΔH^{603} / kJ mol^{-1}	$\Delta H^{*,603}$ / kJ mol^{-1}	$\Delta H^{*,298}$ / kJ mol^{-1}
2.005	t.d.	603	411.6	583.6	428.8
1.807	t.d.	603	417.8	589.8	435.0
2.312	t.d.	603	436.3	608.3	453.5
					Mean 439.1 ± 15

$\Delta H_f^{\ominus}[Pt(PEt_3)_2Cl_2, cis, c] = -(655 \pm 15)$ kJ mol^{-1}
$\Delta H_f^{\ominus}[Pt(PEt_3)_2Cl_2, cis, g] = -(481.6 \pm 21)$ kJ mol^{-1}

$$[Pt(PEt_3)_2Cl_2](c) \longrightarrow PtCl_2(c) + 2PEt_3(g) \quad (1)$$

$$PEt_3(g) + PtCl_2(c) \longrightarrow Pt(c) + PEt_3Cl_2(g) \quad (2)$$

$$PEt_3Cl_2(g) \longrightarrow PEt_2Cl(g) + EtCl(g) \quad (3)$$

was formed on condensation of the hot vapours escaping from the reaction vessel (*e.g.* PEt_4Cl from EtCl and excess PEt_3). We cannot accurately assess the contribution to the measured heat of reaction from the chlorination reactions, as $\Delta H_f^{\ominus}$ values are not available for chlorinated phosphines. For complete chlorination [equation (4)], ΔH_r at 298 K is ~

$$PEt_3(g) + 3Cl_2(g) \longrightarrow PCl_3(g) + 3EtCl(g) \quad (4)$$

−517 kJ mol^{-1}, and is virtually the same at *ca.* 600 K. We have assumed that for the partial chlorination $[PEt_3(g) + Cl_2(g) \longrightarrow$ products (g)], the reaction heat is one-third of that for complete reaction, $\Delta H_r \sim -172$ kJ mol^{-1}.

The measured ΔH^{603} (Table 1), relating to the cell reaction of equation (5) coupled with $\Delta H_r \sim -172$ kJ mol^{-1} for partial chlorination, yields $\Delta H^{*,603} = \Delta H^{603} + 172$ (kJ mol^{-1}) for the formal decomposition [equation (6)], from which $\Delta H^{*,298}$ and $\Delta H_f^{\ominus}[Pt(PEt_3)_2Cl_2, cis, c]$ were derived.

$$\begin{aligned}[Pt(PEt_3)_2Cl_2](cis, c, 298) \longrightarrow {} & Pt(c, 603) + PEt_3(g, 603) + \\ & \text{chlorinated phosphines } (g, 603) \quad (5)\end{aligned}$$

$$\begin{aligned}[Pt(PEt_3)_2Cl_2](cis, c, 298) \longrightarrow {} & \\ & Pt(c, 603) + 2PEt_3(g, 603) + Cl_2(g, 603) \quad (6)\end{aligned}$$

trans-*Dichlorobis(triethylphosphine)platinum*(II), $[Pt(PEt_3)_2Cl_2]$.—Vacuum-sublimation measurements in the calorimeter were made at 431 and 470 K. Thermal-decomposition measurements at 603 K are given in Table 2, and interpreted in the same way as for the *cis* isomer; the products were a strong mirror of platinum in the reaction vessel, and a whitish deposit in the exit-tube. Sublimation studies at 431 K on the *cis* isomer were only partially successful, the sublimation process being slow relative to the *trans* isomer at this temperature.

Table 2. Sublimation and thermal decomposition of *trans*-$[Pt(PEt_3)_2Cl_2]$

Sample mass (mg)	Method	T/K	ΔH_{sub}^{T} / kJ mol^{-1}	ΔH_{sub}^{298} / kJ mol^{-1}
1.210	v.s.	431	210.3	149.3
1.407	v.s.	431	215.9	154.9
1.429	v.s.	431	207.5	146.5
2.742	v.s.	470	228.9	147.4
2.340	v.s.	470	227.7	146.2
				Mean 148.9 ± 3

Sample mass (mg)	Method	T/K	ΔH^{603} / kJ mol^{-1}	$\Delta H^{*,603}$ / kJ mol^{-1}	$\Delta H^{*,298}$ / kJ mol^{-1}
1.909	t.d.	603	401.3	573.3	418.5
1.347	t.d.	603	408.6	580.6	425.8
2.161	t.d.	603	418.2	590.2	435.4
2.207	t.d.	603	408.3	580.3	425.5
1.662	t.d.	603	423.0	595.0	440.2
2.175	t.d.	603	402.7	574.7	419.9
					Mean 427.6 ± 7

$\Delta H_f^{\ominus}[Pt(PEt_3)_2Cl_2, trans, c] = -(643.6 \pm 7)$ kJ mol^{-1}
$\Delta H_f^{\ominus}[Pt(PEt_3)_2Cl_2, trans, g] = -(494.7 \pm 8)$ kJ mol^{-1}

Table 3. Sublimation and thermal decomposition of *trans*-$[Pt(PPr^i_3)_2Cl_2]$

Sample mass (mg)	T/K	Method	ΔH_{sub}^{T} / kJ mol^{-1}	ΔH_{sub}^{298} / kJ mol^{-1}
1.737	478	v.s.	306.4	190.1
1.368	478	v.s.	308.2	191.9
1.817	478	v.s.	303.9	187.6
1.466	478	v.s.	313.5	197.2
1.527	499	v.s.	330.3	198.9
2.131	499	v.s.	325.5	194.1
				Mean 193.3 ± 4

Sample mass (mg)	T/K	Method	ΔH^{T} / kJ mol^{-1}	$\Delta H^{*,T}$ / kJ mol^{-1}	$\Delta H^{*,298}$ / kJ mol^{-1}
2.146	582	t.d.	494.8	682.9	487.8
2.232	582	t.d.	505.1	693.2	498.1
2.910	635	t.d.	551.4	738.9	498.1
2.894	635	t.d.	534.9	722.4	481.6
2.733	635	t.d.	543.6	731.1	490.3
3.353	635	t.d.	530.3	717.8	477.0
					Mean 488.8 ± 7

$\Delta H_f^{\ominus}[Pt(PPr^i_3)_2Cl_2, trans, c] = -(785 \pm 7)$ kJ mol^{-1}
$\Delta H_f^{\ominus}[Pt(PPr^i_3)_2Cl_2, trans, g] = -(592 \pm 8)$ kJ mol^{-1}

trans-*Dichlorobis(tri-isopropylphosphine)platinum*(II), $[Pt(PPr^i_3)_2Cl_2]$.—The vacuum-sublimation microcalorimetric technique was successfully applied at 478 and 499 K, with results as summarized in Table 3. Thermal-decomposition measurements at 582 and 635 K gave a bright platinum mirror in the hot zone and capillary-tube container, and a white solid (water soluble) settled in the cooler exit-tube. Results are interpreted on the same basis as for $[Pt(PEt_3)_2Cl_2]$; the chlorination reaction [equation (7)] is calculated to have

$$PPr^i_3(g) + 3Cl_2(g) \longrightarrow PCl_3(g) + 3Pr^iCl(g) \quad (7)$$

$\Delta H_r \sim -576$ kJ mol^{-1} at 298 K, corresponding to a contribution from partial chlorination of liberated PPr^i_3 in the thermal-decomposition reaction of *ca.* −192 kJ mol^{-1} at

Table 4. Thermal decomposition of *trans*-$[Pt\{P(C_6H_{11})_3\}_2Cl_2]$

Sample mass (mg)	T/K	ΔH^T kJ mol^{-1}	$\Delta H^{*,T}$ kJ mol^{-1}	$\Delta H^{*,298}$ kJ mol^{-1}
2.119	582	712.1	903.1	598.1
3.117	582	708.5	899.5	594.5
2.002	582	690.7	881.7	576.7
3.447	603	736.5	927.5	594.1
2.506	635	769.9	960.9	579.0
2.451	635	785.6	976.6	594.7
				Mean 589.5 ± 8

$\Delta H_f^{\ominus}[Pt\{P(C_6H_{11})_3\}_2Cl_2$, *trans*, c$] = -(999.5 \pm 8)$ kJ mol^{-1}

Table 5. Thermal decomposition of *cis*-$[Pd(PPh_3)_2Cl_2]$

Sample mass (mg)	T/K	ΔH^{603} kJ mol^{-1}	ΔH^{298} kJ mol^{-1}
2.120	603	508.6	250.3
2.207	603	503.4	245.1
2.518	603	512.7	254.4
1.745	603	531.3	273.0
1.923	603	530.7	272.4
1.948	603	522.3	264.0
			Mean 259.9 ± 10

$\Delta H_f^{\ominus}[Pd(PPh_3)_2Cl_2$, *cis*, c$] = 205.3 \pm 10$ kJ mol^{-1}

298 K. (The contribution is reduced to -188 kJ mol^{-1} at 582 K and -187.5 kJ mol^{-1} at 635 K.)

trans-*Dichlorobis(tricyclohexylphosphine)platinum*(II), $[Pt\{P(C_6H_{11})_3\}_2Cl_2]$.—Thermal-decomposition studies were made at 582—635 K, giving a metallic mirror in the reaction vessel, and a white solid which condensed in the exit-tube. The results in Table 4 are interpreted as for $[Pt(PEt_3)_2Cl_2]$; in this case the complete chlorination reaction to form PCl_3(g) and chlorocyclohexane has $\Delta H_r \sim 575$ kJ mol^{-1} at 298 K, reducing to ~ 573 kJ mol^{-1} at temperatures near 600 K. The chlorination contribution to ΔH^T, taken as one third of this, is ~ -191 kJ mol^{-1}.

cis-*Dichlorobis(triphenylphosphine)palladium*(II), $[Pd(PPh_3)_2Cl_2]$.—Thermal-decomposition measurements were made at 603 K. The decomposition products were a black powder remaining in the capillary-tube container, and a liquid condensate (with some white solid) in the cooler exit-tube. The measured ΔH^{603}, listed in Table 5, are attributed to the primary decomposition of equation (8).

$$[Pd(PPh_3)_2Cl_2](cis, \text{c}, 298) \longrightarrow PdCl_2(\text{c}, 603) + 2PPh_3(\text{g}, 603) \quad (8)$$

cis-*Dichlorobis(triphenylphosphine)platinum*(II), $[Pt(PPh_3)_2Cl_2]$.—Thermal decomposition was incomplete at temperatures below 600 K. In the range 620—675 K, decomposition left a black residue in the capillary-tube container, black spots on the wall of the reaction vessel, and the exit-tube was clean. On pumping out the hot reaction vessel, a slight white dust settled in the cool exit-tube. The results (Table 6) are interpreted in terms of the primary decomposition of equation (9)

$$[Pt(PPh_3)_2Cl_2](cis, \text{c}) \longrightarrow PtCl_2(\text{c}, T) + 2PPh_3(\text{g}, T) \quad (9)$$

on the assumption that chlorination of the phosphine was only slight at these temperatures.

Table 6. Thermal decomposition of *cis*-$[Pt(PPh_3)_2Cl_2]$

Sample mass (mg)	T/K	ΔH^T kJ mol^{-1}	ΔH^{298} kJ mol^{-1}
2.437	620	588.6	311.4
1.802	620	585.2	307.9
2.699	620	596.0	318.8
1.811	675	658.5	320.3
			Mean 314.6 ± 6

$\Delta H_f^{\ominus}[Pt(PPh_3)_2Cl_2$, *cis*, c$] = 173 \pm 6$ kJ mol^{-1}

Table 7. Thermal decomposition of *cis*-$[Pt(PMe_2Ph)_2Cl_2]$

Sample mass (mg)	T/K	ΔH^T kJ mol^{-1}	$\Delta H^{*,T}$ kJ mol^{-1}	$\Delta H^{*,298}$ kJ mol^{-1}
1.466	670	398.2	545.2	353.2
2.688	670	394.7	541.7	349.7
1.621	623	371.2	518.2	356.0
2.058	623	371.3	518.3	356.1
				Mean 353.8 ± 5

$\Delta H_f^{\ominus}[Pt(PMe_2Ph)_2Cl_2$, *cis*, c$] = -(280 \pm 5)$ kJ mol^{-1}

Table 8. Thermal decomposition of *cis*-$[Pd(cod)Cl_2]$

Sample mass (mg)	T/K	ΔH^T kJ mol^{-1}	ΔH^{298} kJ mol^{-1}
2.954	473	171.9	128.1
2.582	473	172.4	128.6
3.256	532	192.2	130.6
3.105	532	191.8	130.2
2.938	532	192.1	130.5
2.632	532	191.1	129.5
3.055	532	192.5	130.9
			Mean 129.8 ± 0.8

$\Delta H_f^{\ominus}[Pd(cod)Cl_2$, *cis*, c$] = -(234.4 \pm 1)$ kJ mol^{-1}

cis-*Dichlorobis(dimethylphenylphosphine)platinum*(II), $[Pt(PMe_2Ph)_2Cl_2]$.—Thermal-decomposition measurements were made at 623 and 670 K; a white powder settled in the exit-tube and the residue in the hot zone and capillary tube was shiny black. The measured ΔH^T include the contribution from partial chlorination of the liberated phosphine; for the reaction $PMe_2Ph + 3Cl_2 \longrightarrow PhCl + 2MeCl + PCl_3$, $\Delta H_r \sim -439.2$ kJ mol^{-1} at 298 K. Allowing $\Delta H_r/3$ for the chlorination $PMe_2Ph + Cl_2 \longrightarrow$ products in the hot zone, the correction is ~ -147 kJ mol^{-1} at temperature $T \sim 600$ K. Results are summarised in Table 7.

cis-*Dichloro(cyclo-octa-*1,5-*diene)palladium*(II), $[Pd(cod)Cl_2]$.—Thermal-decomposition measurements were made at 473 and at 532 K, leaving a black deposit in the reaction vessel and capillary tube. The exit-tube was clean, with traces of colourless liquid. Results are summarized in Table 8, and relate to the disruption reaction of equation (10).

$$[Pd(cod)Cl_2](cis, \text{c}, 298) \longrightarrow \text{cod}(\text{g}, T) + PdCl_2(\text{c}, T) \quad (10)$$

cis-*Dichloro(cyclo-octa-*1,5-*diene)platinum*(II), $[Pt(cod)Cl_2]$.—Thermal-decomposition studies at 583—603 K gave a black, shiny deposit in the capillary-tube container, and black spots on the wall of the reaction vessel. The exit-tube was

Table 9. Thermal decomposition of *cis*-[Pt(cod)Cl$_2$]

Sample mass (mg)	T/K	ΔH^T kJ mol^{-1}	ΔH^{298} kJ mol^{-1}
1.869	583	223.2	146.8
2.665	583	218.1	141.7
1.621	583	219.3	142.9
2.083	603	244.7	161.9
			Mean 148.3 ± 9

$\Delta H_f^{\ominus}$[Pt(cod)Cl$_2$, *cis*, c] = −(240.8 ± 9) kJ mol^{-1}

Table 10. Sublimation and thermal decomposition of *cis*-[Pt(PEt$_3$)$_2$Me$_2$]

Sample mass (mg)	Method	T/K	ΔH^T kJ mol^{-1}	ΔH^{298} kJ mol^{-1}
2.132	v.s.	403	174.5	127.0
2.285	v.s.	403	184.0	136.5
2.116	v.s.	443	198.6	129.2
			Mean ΔH_{sub}^{298} = 130.9 ± 6 kJ mol^{-1}	
2.257	t.d.	573	368.2	221.5
2.093	t.d.	573	364.1	217.4
2.312	t.d.	573	380.4	233.7
1.681	t.d.	573	366.8	220.1
1.652	t.d.	573	356.2	209.5
1.202	t.d.	573	366.0	219.3
			Mean ΔH^{298} = 220.3 ± 6 kJ mol^{-1}	

$\Delta H_f^{\ominus}$[Pt(PEt$_3$)$_2$Me$_2$, *cis*, c] = −(520 ± 6) kJ mol^{-1}
$\Delta H_f^{\ominus}$[Pt(PEt$_2$)$_2$Me$_2$, *cis*, g] = −(389 ± 8) kJ mol^{-1}

clean. The measured ΔH^T (Table 9) are related to the presumed decomposition reaction of equation (11).

$$[\mathrm{Pt(cod)Cl_2}](cis,\ \mathrm{c},\ 298) \longrightarrow \tfrac{1}{2}[\mathrm{Pt(c)} + \mathrm{PtCl_2(c)}](T) + \tfrac{1}{2}[\mathrm{cod(g)} + \mathrm{C_8H_{12}Cl_2(g)}](T) \quad (11)$$

cis-*Dimethylbis(triethylphosphine)platinum*(II), [Pt(PEt$_3$)$_2$Me$_2$].—Sublimation and thermal-decomposition results are summarized in Table 10. The ΔH^T values are related to the presumed hot-zone decomposition [equation (12)].

$$[\mathrm{Pt(PEt_3)_2Me_2}](cis,\ \mathrm{c},\ 298) \longrightarrow \mathrm{Pt(c,\ 573)} + (2\mathrm{PEt_3} + \mathrm{C_2H_6})(\mathrm{g},\ 573) \quad (12)$$

cis-*Bis*(o-*tolyl*)*bis*(*triethylphosphine*)*platinum*(II), [Pt(PEt$_3$)$_2$(C$_6$H$_4$Me-*o*)$_2$].—The vacuum-sublimation microcalorimetric technique was applied satisfactorily at 423 K; thermal-decomposition measurements at 623 K gave a platinum mirror in the reaction zone, and a liquid condensate in the cooler exit-tube. The measured ΔH^T values are summarized in Table 11 and related to the presumed hot-zone reaction [equation (13)].

$$[\mathrm{Pt(PEt_3)_2(C_6H_4Me\text{-}}o)_2](cis,\ \mathrm{c},\ 298) \longrightarrow \mathrm{Pt}(\mathrm{c},\ T) + [2\mathrm{PEt_3} + \mathrm{C_6H_5(CH_2)_2C_6H_5}](\mathrm{g},\ T) \quad (13)$$

cis-*Chloro*(*methyl*)*bis*(*triethylphosphine*)*platinum*(II), [Pt(PEt$_3$)$_2$(CH$_3$)Cl].—Thermal-decomposition measurements at 617 K are given in Table 12; a platinum mirror formed in the reaction vessel, and a white solid settled in the exit-tube.

Table 11. Sublimation and thermal decomposition of *cis*-[Pt(PEt$_3$)$_2$(C$_6$H$_4$Me-*o*)$_2$]

Sample mass (mg)	Method	T/K	ΔH^T kJ mol^{-1}	ΔH^{298} kJ mol^{-1}
1.202	v.s.	423	265.1	182.5
1.373	v.s.	423	269.3	186.7
1.311	v.s.	423	263.1	180.5
			Mean ΔH_{sub}^{298} = 183.2 ± 4 kJ mol^{-1}	
2.001	t.d.	623	511.0	254.3
1.693	t.d.	623	492.6	235.9
2.063	t.d.	623	535.0	278.3
			Mean ΔH^{298} = 256.2 ± 24 kJ mol^{-1}	

$\Delta H_f^{\ominus}$[Pt(PEt$_3$)$_2$(C$_6$H$_4$Me-*o*)$_2$, *cis*, c] = −(329 ± 24) kJ mol^{-1}
$\Delta H_f^{\ominus}$[Pt(PEt$_3$)$_2$(C$_6$H$_4$Me-*o*)$_2$, *cis*, g] = −(146 ± 24) kJ mol^{-1}

Table 12. Thermal decomposition of *cis*-[Pt(PEt$_3$)$_2$(CH$_3$)Cl]

Sample mass (mg)	T/K	ΔH^{617} kJ mol^{-1}	ΔH^{298} kJ mol^{-1}
2.097	617	445.2	276.1
2.051	617	440.2	271.1
2.430	617	432.9	263.8
2.038	617	441.5	272.4
			Mean 270.9 ± 5

$\Delta H_f^{\ominus}$[Pt(PEt$_3$)$_2$(CH$_3$)Cl, *cis*, c] = −(569 ± 5) kJ mol^{-1}

Table 13. Thermal decomposition of *cis*-[Pt(PEt$_3$)$_2$(C$_6$H$_4$Me-*o*)Cl]

Sample mass (mg)	T/K	ΔH^T kJ mol^{-1}	ΔH^{298} kJ mol^{-1}
2.060	606	508.6	310.3
1.501	606	474.2	275.9
2.225	606	503.4	305.1
1.536	606	497.8	299.5
			Mean 297.7 ± 15

$\Delta H_f^{\ominus}$[Pt(PEt$_3$)$_2$(C$_6$H$_4$Me-*o*)Cl, *cis*, c] = −(495 ± 15) kJ mol^{-1}

Results are evaluated in terms of the presumed cell reaction [equation (14)].

$$[\mathrm{Pt(PEt_3)_2(CH_3)Cl}](cis,\ \mathrm{c},\ 298) \longrightarrow \mathrm{Pt(c,\ 617)} + (2\mathrm{PEt_3} + \mathrm{CH_3Cl})(\mathrm{g},\ 617) \quad (14)$$

cis-*Chloro*(o-*tolyl*)*bis*(*triethylphosphine*)*platinum*(II), [Pt(PEt$_3$)$_2$(C$_6$H$_4$Me-*o*)Cl].—Thermal-decomposition measurements were made at 606 K; a platinum mirror formed in the reaction vessel and capillary-tube container, and a white solid settled in the exit-tube. In the coolest part (near the end) of the exit, a colourless liquid condensed on the surface. The measured ΔH^T (Table 13) are interpreted for the presumed hot-zone reaction [equation (15)].

$$[\mathrm{Pt(PEt_3)_2(C_6H_4Me\text{-}}o)\mathrm{Cl}](cis,\ \mathrm{c},\ 298) \longrightarrow \mathrm{Pt(c,\ 606)} + (2\mathrm{PEt_3} + \mathrm{C_6H_5CH_2Cl})(\mathrm{g},\ 606) \quad (15)$$

cis-*Bis*(*ethylthio*)*bis*(*triethylphosphine*)*platinum*(II), [Pt(PEt$_3$)$_2$(SEt)$_2$].—Sublimation measurements at 426 K, and thermal-decomposition studies over the range 593—677 K are summarized in Table 14. The decomposition led to a platinum mirror in the reaction zone, and some white product

Table 14. Sublimation and thermal decomposition of *cis*-[Pt(PEt$_3$)$_2$(SEt)$_2$]

Sample mass (mg)	Method	T/K	ΔH^T / kJ mol^{-1}	ΔH^{298} / kJ mol^{-1}
1.381	v.s.	426	276.9	201.4
1.913	v.s.	426	265.5	190.0
	Mean ΔH_{sub}^{298} = 195.7 ± 11 kJ mol^{-1}			
2.049	t.d.	593	460.4	249.7
2.033	t.d.	593	449.2	238.5
2.109	t.d.	593	447.0	236.3
2.297	t.d.	593	463.4	252.7
1.753	t.d.	677	514.1	228.0
	Mean ΔH^{298} = 241.0 ± 9 kJ mol^{-1}			

ΔH_f°[Pt(PEt$_3$)$_2$(SEt)$_2$, *cis*, c] = −(650.5 ± 9) kJ mol^{-1}

ΔH_f°[Pt(PEt$_3$)$_2$(SEt)$_2$, *cis*, g] = −(455 ± 14) kJ mol^{-1}

Table 15. Thermal decomposition of *cis*-[Pt(PPh$_3$)$_2$(SEt)$_2$]

Sample mass (mg)	T/K	ΔH^T / kJ mol^{-1}	ΔH^{298} / kJ mol^{-1}
2.459	637	596.8	250.6
2.008	637	581.6	235.4
1.955	637	615.8	269.6
1.981	677	638.2	240.2
2.019	677	667.8	269.8
			Mean 253.1 ± 14

ΔH_f°[Pt(PPh$_3$)$_2$(SEt)$_2$, *cis*, c] = 181.6 ± 14 kJ mol^{-1}

in the exit-tube. Results are interpreted in terms of the presumed hot-zone reaction [equation (16)].

$$[\mathrm{Pt(PEt_3)_2(SEt)_2}](cis,\ \mathrm{c},\ 298) \longrightarrow \mathrm{Pt(c},\ T) + [\mathrm{PEt_3} + \mathrm{P(S)Et_3} + \mathrm{SEt_2}](\mathrm{g},\ T) \quad (16)$$

cis-*Bis(ethylthio)bis(triphenylphosphine)platinum*(II), [Pt(PPh$_3$)$_2$(SEt)$_2$].—Thermal-decomposition measurements were made at 637 and 677 K, giving a blackened capillary tube and some spots of platinum metal in the hot-zone, and a colourless liquid and white solid in the exit-tube. The measured ΔH^T are interpreted as for [Pt(PEt$_3$)$_2$(SEt)$_2$], presuming that liberated PPh$_3$ abstracts sulphur from the SEt fragments to form P(S)Ph$_3$ [equation (17)].

$$[\mathrm{Pt(PPh_3)_2(SEt)_2}](cis,\ \mathrm{c},\ 298) \longrightarrow \mathrm{Pt(c},\ T) + [\mathrm{PPh_3} + \mathrm{P(S)Ph_3} + \mathrm{SEt_2}](\mathrm{g},\ T) \quad (17)$$

cis-*Dichlorobis(methyl cyanide)palladium*(II), [Pd(MeCN)$_2$Cl$_2$].—Thermal-decomposition studies were made over the range 532—588 K; the residue in the capillary tube and reaction zone was a red-brown powder, and the exit-tube was clean. The vacuum-sublimation technique was applied at 396 K, but led to decomposition of the complex, and formation of a red solid, as at higher temperatures. Results are summarized in Table 16, and interpreted in terms of the primary decomposition [equation (18)].

$$[\mathrm{Pd(MeCN)_2Cl_2}](cis,\ \mathrm{c},\ 298) \longrightarrow \mathrm{PdCl_2(c},\ T) + 2\mathrm{MeCN(g},\ T) \quad (18)$$

cis-*Tetrachlorobis(triethylphosphine)platinum*(IV), [Pt(PEt$_3$)$_2$Cl$_4$].—Thermal-decomposition measurements at 606 K are given in Table 17. The decomposition gave a black residue in the reaction zone, and a white product settled with a colourless liquid in the cooler exit-tube. The measured ΔH^{606} (Table 17) include the contribution from chlorination of liberated PEt$_3$, for which correction is made as in the case of [Pt(PEt$_3$)$_2$Cl$_2$], to give $\Delta H^{*,606}$ for the decomposition [equation (19)].

Table 16. Thermal decomposition of *cis*-[Pd(MeCN)$_2$Cl$_2$]

Sample mass (mg)	T/K	ΔH^T / kJ mol^{-1}	ΔH^{298} / kJ mol^{-1}
2.249	532	185.1	138.0
2.386	532	179.3	132.3
2.750	532	176.8	129.8
2.383	569	184.6	129.2
2.527	569	184.2	128.8
2.333	588	195.9	136.2
2.199	588	194.9	135.2
			Mean 132.8 ± 3

ΔH_f°[Pd(MeCN)$_2$Cl$_2$, *cis*, c] = −(148.8 ± 3) kJ mol^{-1}

Table 17. Thermal decomposition of *cis*-[Pt(PEt$_3$)$_2$Cl$_4$]

Sample mass (mg)	T/K	ΔH^{606} / kJ mol^{-1}	$\Delta H^{*,606}$ / kJ mol^{-1}	$\Delta H^{*,298}$ / kJ mol^{-1}
1.903	606	478.0	822.0	654.3
2.535	606	469.5	813.5	645.8
2.382	606	480.0	824.0	656.3
2.100	606	465.6	809.6	641.9
2.055	606	461.6	805.6	637.9
				Mean 647.2 ± 7

ΔH_f°[Pt(PEt$_3$)$_2$Cl$_4$, *cis*, c] = −(863 ± 7) kJ mol^{-1}

$$[\mathrm{Pt(PEt_3)_2Cl_4}](cis,\ \mathrm{c},\ 298) \longrightarrow \mathrm{Pt(c},\ 606) + 2\mathrm{PEt_3(g},\ 606) + 2\mathrm{Cl_2(g},\ 606) \quad (19)$$

Discussion

The collected results of the present studies are summarized in Table 18, which lists values for ΔH_f°(c), ΔH_{sub}°, and ΔH_f°(g) for the various complexes. We could not measure the sublimation heats of many of these compounds, and those which carry an asterisk are estimates only, considered uncertain by at least ±20 kJ mol^{-1}. The estimated values were obtained by extrapolation of linear plots of ΔH_{sub} *versus* molecular weight; the line through the points for [Pt(PEt$_3$)$_2$Me$_2$] and [Pt(PEt$_3$)$_2$(C$_6$H$_4$Me-*o*)$_2$] served to draw a parallel line through the point for *cis*-[Pt(PEt$_3$)$_2$Cl$_2$] which was used to obtain values for *cis*-[PtL$_2$Cl$_2$] compounds. A line through *trans*-[Pt(PEt$_3$)$_2$Cl$_2$] and *trans*-[Pt(PPr$^i_3$)$_2$Cl$_2$] was extended to obtain ΔH_{sub} for *trans*-[Pt{P(C$_6$H$_{11}$)$_3$}$_2$Cl$_2$]. The values accepted for the complexes of PdCl$_2$ are probably less reliable; available experimental data indicate that ΔH_{sub} for PdCl$_2$ is larger than that for PtCl$_2$ by *ca.* 40 kJ mol^{-1}. We have presumed that the sublimation heats of [PdL$_2$Cl$_2$] may be higher than those of the corresponding [PtL$_2$Cl$_2$] by 10 kJ mol^{-1}.

The uncertainty attached to each ΔH_f°(g) value includes uncertainties of our measurements, but not of auxiliary data. (For the purpose of bond-energy calculations this omission is not significant). Table 19 gives derived values, ΔH_D(g), for complexes containing PtCl$_2$ or PdCl$_2$, and values of ΔH_{diss} for all complexes. The enthalpies of ligand disruption, ΔH_D(g), refer to equation (20a) or (20b), accepting available

$$[\mathrm{PtL_2Cl_2}](\mathrm{g}) \longrightarrow 2\mathrm{L(g)} + \mathrm{PtCl_2(g)} \quad (20a)$$

$$[\mathrm{PdL_2Cl_2}](\mathrm{g}) \longrightarrow 2\mathrm{L(g)} + \mathrm{PdCl_2(g)} \quad (20b)$$

Table 18. Collected values of $\Delta H_f^{\ominus}$(c), $\Delta H_{sub}^{\ominus}$, and $\Delta H_f^{\ominus}$(g)

Compound	$\Delta H_f^{\ominus}$(c) / kJ mol^{-1}	$\Delta H_{sub}^{\ominus}$ / kJ mol^{-1}	$\Delta H_f^{\ominus}$(g) / kJ mol^{-1}
cis-[Pt(PEt$_3$)$_2$Cl$_2$]	−(655 ± 15)	174 ± 16	−(482 ± 21)
trans-[Pt(PEt$_3$)$_2$Cl$_2$]	−(644 ± 7)	149 ± 3	−(495 ± 8)
trans-[Pt(PPr$^i_3$)$_2$Cl$_2$]	−(785 ± 7)	193 ± 4	−(592 ± 8)
trans-[Pt{P(C$_6$H$_{11}$)$_3$}$_2$Cl$_2$]	−(999 ± 8)	300 *	−(699 ± 21)
cis-[Pd(PPh$_3$)$_2$Cl$_2$]	205 ± 10	285 *	490 ± 22
cis-[Pt(PPh$_3$)$_2$Cl$_2$]	173 ± 6	275 *	448 ± 21
cis-[Pt(PMe$_2$Ph)$_2$Cl$_2$]	−(280 ± 5)	185 *	−(95 ± 21)
cis-[Pd(cod)Cl$_2$]	−(234 ± 1)	140 *	−(96 ± 20)
cis-[Pt(cod)Cl$_2$]	−(241 ± 9)	130 *	−(111 ± 22)
cis-[Pt(PEt$_3$)$_2$Me$_2$]	−(520 ± 6)	131 ± 6	−(389 ± 8)
cis-[Pt(PEt$_3$)$_2$(C$_6$H$_4$Me-*o*)$_2$]	−(329 ± 24)	183 ± 4	−(146 ± 24)
cis-[Pt(PEt$_3$)$_2$(CH$_3$)Cl]	−(569 ± 5)	152 *	−(417 ± 21)
cis-[Pt(PEt$_3$)$_2$(C$_6$H$_4$Me-*o*)Cl]	−(495 ± 15)	179 *	−(316 ± 25)
cis-[Pt(PEt$_3$)$_2$(SEt)$_2$]	−(651 ± 9)	196 ± 11	−(455 ± 14)
cis-[Pt(PPh$_3$)$_2$(SEt)$_2$]	182 ± 14	295 *	477 ± 25
cis-[Pd(MeCN)$_2$Cl$_2$]	−(149 ± 3)	132 *	−(17 ± 20)
cis-[Pt(PEt$_3$)$_2$Cl$_4$]	−(863 ± 7)	200 *	−(663 ± 21)

Table 19. Values of $\Delta H_D^{\ominus}$(g) and $\Delta H_{diss}^{\ominus}$

Compound	$\Delta H_D^{\ominus}$(g) / kJ mol^{-1}	$\Delta H_{diss}^{\ominus}$ / kJ mol^{-1}
cis-[Pt(PEt$_3$)$_2$Cl$_2$]	376 ± 21	1 073 ± 21
trans-[Pt(PEt$_3$)$_2$Cl$_2$]	390 ± 8	1 087 ± 8
cis-[Pt(PEt$_3$)$_2$(CH$_3$)Cl]		1 032 ± 21
cis-[Pt(PEt$_3$)$_2$Me$_2$]		1 027 ± 10
cis-[Pt(PEt$_3$)$_2$(C$_6$H$_4$Me-*o*)Cl]		1 086 ± 28
cis-[Pt(PEt$_3$)$_2$(C$_6$H$_4$Me-*o*)$_2$]		1 094 ± 29
cis-[Pt(PEt$_3$)$_2$(SEt)$_2$]		1 017 ± 20
cis-[Pt(PEt$_3$)$_2$Cl$_4$]		1 496 ± 21
trans-[Pt(PPr$^i_3$)$_2$Cl$_2$]	406 ± 8	1 104 ± 8
trans-[Pt{P(C$_6$H$_{11}$)$_3$}$_2$Cl$_2$]	399 ± 21	1 097 ± 21
cis-[Pt(PMe$_2$Ph)$_2$Cl$_2$]	279 ± 21	977 ± 21
cis-[Pt(PPh$_3$)$_2$Cl$_2$]	291 ± 21	986 ± 21
cis-[Pt(PPh$_3$)$_2$(SEt)$_2$]		929 ± 29
cis-[Pt(cod)Cl$_2$]	280 ± 22	978 ± 22
cis-[Pd(cod)Cl$_2$]	283 ± 20	769 ± 20
cis-[Pd(PPh$_3$)$_2$Cl$_2$]	266 ± 22	753 ± 22
cis-[Pd(MeCN)$_2$Cl$_2$]	293 ± 20	780 ± 20

values,[22] $\Delta H_f^{\ominus}$(PtCl$_2$, g) ~ 110.5 kJ mol^{-1}, and [13] $\Delta H_f^{\ominus}$(PdCl$_2$, g) ~ 128 kJ mol^{-1}. The enthalpies of dissociation ΔH_{diss} to form gaseous metal atoms and free ligand species refer to the total disruption process given by equation (21) (or its equivalent for other Pt and Pd complexes).

$$[\mathrm{PtL_2X_2}](\mathrm{g}) \longrightarrow 2\mathrm{L(g)} + \mathrm{Pt(g)} + 2\mathrm{X(g)} \qquad (21)$$

The $\Delta H_{diss}^{\ominus}$ values were derived using the following $\Delta H_f^{\ominus}$(g) for ligands X, and for Pt(g) and Pd(g) (kJ mol^{-1}): Pt(g) = 565.7 ± 4;[13] Pd(g) = 372.4 ± 4;[13] Cl(g) = 121.3 ± 0.01;[23] CH$_3$(g) = 144 ± 3;[24] C$_6$H$_4$Me-*o*(g) = 299 ± 12 [estimated assuming D(H–C$_6$H$_4$Me) = D(H–C$_6$H$_5$)];[25] SEt(g) = 106 ± 10.[26]

The values $\Delta H_D^{\ominus}/2$ provide a measure of the bonding power of the various donor ligands to PtCl$_2$ or PdCl$_2$. These indicate decreasing ligand bonding power to PtCl$_2$ in the sequence PPr$^i_3$ $\gtrsim$ P(C$_6$H$_{11}$)$_3$ $\gtrsim$ PEt$_3$ > PPh$_3$ $\gtrsim$ PMe$_2$Ph ~ ½(cod).

From a previous study,[5] we may add: ½(cod) > pyridine > NH$_2$Pr^i > NH$_2$Me > NH$_3$. The few available data on [PdL$_2$Cl$_2$] complexes suggest that ligands bind to PdCl$_2$ with similar power as to PtCl$_2$.

The values $\Delta H_{diss}^{\ominus}$ provide '*bond-enthalpy contributions*' of the metal–ligand and metal–X bonds in a complex [PtL$_2$X$_2$], on the basis of bond additivity [equation (22)].

$$\Delta H_{diss}^{\ominus}[\mathrm{PtL_2X_2}] = 2\bar{E}(\mathrm{Pt{-}L}) + 2\bar{E}(\mathrm{Pt{-}X}) \qquad (22)$$

The analysis in Table 20 is derived from the acceptance of a constant transferable $\bar{E}$(Pt–Cl) = 290 kJ mol^{-1}, which is less than the mean bond-dissociation enthalpy, $\bar{D}$(Pt–Cl) = 349 kJ mol^{-1} in gaseous PtCl$_2$, and in gaseous PtCl$_3$ (295 kJ mol^{-1}),[22] but larger than in Pt$_6$Cl$_{12}$ (g), where $\bar{D}$(Pt–Cl) ~ 229 kJ mol^{-1}.[27] {The crystal-structure analysis of discrete Pt$_6$Cl$_{12}$ groups in PtCl$_2$ by Broderson *et al.*[28] showed each Pt to be bonded to four Cl atoms, with Pt–Cl bond lengths in the range 2.34—2.39 Å: these are longer than in *trans*-[Pt(PEt$_3$)$_2$Cl$_2$], where Messmer and Amma [29] found Pt–Cl ~ 2.29 Å. Bond lengths in the gaseous molecules PtCl$_2$, PtCl$_3$, and PtCl$_4$ have not been measured.}

The choice $\bar{E}$(Pd–Cl) ~ 215 kJ mol^{-1} is also less than $\bar{D}$(Pd–Cl) ~ 243 kJ mol^{-1} in PdCl$_2$(g), and larger than in Pd$_5$Cl$_{10}$(g), where $\bar{D}$ ~ 182 kJ mol^{-1}.[26]

The main conclusions drawn from Table 20 are as follows. (*i*) The trialkylphosphine ligands bind more firmly to PtCl$_2$ than do amines, consistent with the view that the P ⟶ Pt donor bond is supplemented by back co-ordination from filled *d* orbitals on Pt: the short [29] Pt–P bond length (2.3 Å) in *trans*-[Pt(PEt$_3$)$_2$Cl$_2$] relative to the single bond length (2.41 Å) also indicates some double-bond character, $\mathrm{Pt} \rightleftarrows \mathrm{P}$. (*ii*) The contribution $\bar{E}$(PPh$_3$ ⟶ Pt) is less than for alkylphosphine ligands, and steric crowding may be a contributory factor. The lower value for $\bar{E}$(PMe$_2$Ph ⟶ Pt), however, suggests that the phenyl group attached to P is the main cause of reduced ligand power. (*iii*) The contribution $\bar{E}$(|| ⟶ Pt) from cod, of similar magnitude to $\bar{E}$(PPh$_3$ ⟶ Pt), may be augmented by back-co-ordination from Pt to vacant antibonding orbitals of the olefin. There is however, a substantial reorganization of the olefin on its dissociation from the complex, and the $\bar{E}$ value is influenced by this. {In the complex [Ni(cod)$_2$], the formal C=C bonds are longer by *ca.* 0.05 Å than in the free ligand.[30]} The contribution $\bar{E}$(|| ⟶ Pt) from ethylene in [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] is likewise influenced, probably more so, by reorganization of the ethylene ligand on dissociation. (The C=C bond in the complex [31] is *ca.* 0.09 Å longer than in free ethylene.) The contribution $\bar{E}$(||| ⟶ Pt) from diphenylacetylene in [Pt(PPh$_3$)$_2$(PhC≡CPh)] includes a reorganization energy of the formal C≡C bond, which is longer in the analogous [Pt(PhC≡CPh)$_2$] complex [32] by *ca.* 0.08 Å than in the free

Table 20. Bond-enthalpy contributions, $\bar{E}(L \longrightarrow Pt)$ (kJ mol^{-1}) and $\bar{E}(Pt{-}X)$ (kJ mol^{-1})

Basis	Compound	Derived $\bar{E}(L \longrightarrow Pt)$
$\bar{E}(Pt{-}Cl) = 290$	*trans*-$[Pt(PPr^i_3)_2Cl_2]$	$PPr^i_3 \longrightarrow Pt = 262 \pm 4$
	trans-$[Pt\{P(C_6H_{11})_3\}Cl_2]$	$P(C_6H_{11})_3 \longrightarrow Pt = 258.5 \pm 10$
	trans-$[Pt(PEt_3)_2Cl_2]$	$PEt_3 \longrightarrow Pt = 253.5 \pm 4$
	cis-$[Pt(PEt_3)_2Cl_2]$	$PEt_3 \longrightarrow Pt = 246.5 \pm 10$
	cis-$[Pt(PPh_3)_2Cl_2]$	$PPh_3 \longrightarrow Pt = 203 \pm 10$
	cis-$[P(PMe_2Ph)_2Cl_2]$	$PMe_2Ph \longrightarrow Pt = 199 \pm 10$
	$[Pt(cod)Cl_2]$	$\| \longrightarrow Pt = 199 \pm 11$
	cis-$[Pt(NC_5H_5)_2Cl_2]$	$NC_5H_5 \longrightarrow Pt \sim 181 \pm 8$
	cis-$[Pt(NH_2Pr^i)_2Cl_2]$	$NH_2Pr^i \longrightarrow Pt \sim 177 \pm 8$
	cis-$[Pt(NH_2Me)_2Cl_2]$	$NH_2Me \longrightarrow Pt \sim 167 \pm 8$
	cis-$[Pt(NH_3)_2Cl_2]$	$NH_3 \longrightarrow Pt \sim 156 \pm 8$
$\bar{E}(PEt_3 \longrightarrow Pt) = 246.5$	*cis*-$[Pt(PEt_3)_2Me_2]$	$Pt{-}CH_3 = 267 \pm 5$
	cis-$[Pt(PEt_3)_2(C_6H_4Me\text{-}o)_2]$	$Pt{-}C_6H_4Me\text{-}o = 300 \pm 15$
	cis-$[Pt(PEt_3)_2(SEt)_2]$	$Pt{-}SEt = 262 \pm 10$
	$[Pt(PEt_3)_2(CH_3)Cl]$	$Pt{-}CH_3 = 249 \pm 10$
	$[Pt(PEt_3)_2(C_6H_4Me\text{-}o)Cl]$	$Pt{-}C_6H_4Me\text{-}o = 303 \pm 14$
$\bar{E}(PPh_3 \longrightarrow Pt) = 203$	*cis*-$[Pt(PPh_3)_2(SEt)_2]$	$Pt{-}SEt = 262 \pm 15$
	$[Pt(PPh_3)_2(PhC{\equiv}CPh)]$[a]	$||| \longrightarrow Pt = 182 \pm 26$
	$[Pt(PPh_3)_2(CH_2{=}CH_2)]$[b]	$\| \longrightarrow Pt = 154 \pm 28$
$\bar{E}(Pd{-}Cl) = 215$	*cis*-$[Pd(MeCN)_2Cl_2]$	$MeCN \longrightarrow Pd = 175 \pm 10$
	cis-$[Pd(cod)Cl_2]$	$\| \longrightarrow Pd = 169 \pm 10$
	cis-$[Pd(PPh_3)_2Cl_2]$	$PPh_3 \longrightarrow Pd = 162 \pm 10$
$\bar{E}(PEt_3 \longrightarrow Pt) = 246.5$ or	$[Pt(PEt_3)_2Cl_4]$	$Pt{-}Cl = 125 \pm 5$
$\bar{E}(Pt{-}Cl) = 290$		$PEt_3 \longrightarrow Pt = 168 \pm 10$

[a] A. Evans, C. T. Mortimer, and R. J. Puddephat, *J. Organomet. Chem.*, 1975, **96**, C58; coupled with the present value for $\Delta H_f^{\ominus}[Pt(PPh_3)_2Cl_2, c]$ gives $\Delta H_f^{\ominus}(c) = 731.5 \pm 16$ kJ mol^{-1}. We have estimated $\Delta H_{sub} \sim 285 \pm 20$ kJ mol^{-1}, to obtain $\Delta H_f^{\ominus}(g) = 1\,016.5 \pm 26$ and $\Delta H_{diss} = 588 \pm 26$ kJ mol^{-1}. [b] A. Evans, C. T. Mortimer, and R. J. Puddephat, *J. Organomet. Chem.*, 1975, **85**, 101; coupled with $\Delta H_f^{\ominus}[Pt(PPh_3)_2(C_2Ph_2)]$ from the reference in footnote *a* and our estimate, $\Delta H_{sub} \sim 230 \pm 20$ kJ mol^{-1}, to obtain $\Delta H_f^{\ominus}(g) = 686 \pm 28$ and $\Delta H_{diss} = 560 \pm 28$ kJ mol^{-1}.

ligand. These CC bond length changes alone correspond to reorganization energies of the order[33] 50 (cod), 110 (C_2H_4), and 120 kJ mol^{-1} ($PhC{\equiv}CPh$). Addition of these ' reorganization ' energies to the $\bar{E}$ values places the ' ligand bonding power ' in the order $||| \longrightarrow Pt > \| \longrightarrow Pt > \|$ (in cod) $\longrightarrow Pt$, and nearer to the strength of a Pt–C bond. (*iv*) The contribution $\bar{E}(Pt{-}C)$ for attachment to trigonal carbon (Pt–Ph or Pt–C_6H_4Me-*o*) is larger than for attachment to $-CH_3$; the difference reflects that between the bond dissociation enthalpies, $D(Ph{-}H) - D(CH_3{-}H) \sim 30$ kJ mol^{-1}. (*v*) The contribution $\bar{E}(Pt{-}SEt)$ is weaker than $\bar{E}(Pt{-}Cl)$, and of similar magnitude to $\bar{E}(Pt{-}CH_3)$. (*vi*) In the octahedral complex $[Pt(PEt_3)_2Cl_4]$, retention of the $\bar{E}(PEt_3 \longrightarrow Pt)$ value requires a reduced value for $\bar{E}(Pt{-}Cl)$, and *vice versa*. (*vii*) The values $\bar{E}(PPh_3 \longrightarrow Pd)$ and $\bar{E}(\| \longrightarrow Pd)$ are lower by 30—40 kJ mol^{-1} than the corresponding $\bar{E}$ values to Pt; $\bar{E}(MeCN \longrightarrow Pd)$ is slightly less than $\bar{E}(NC_5H_5 \longrightarrow Pt)$; data on $MeCN \longrightarrow Pt$ complexes are not available for direct comparison.

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