

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, $\Delta H_f^\circ(c)/\text{kJ mol}^{-1}$ of the crystalline compounds: *cis*-[Pt(PEt₃)₂Cl₂] = $-(655 \pm 15)$; *trans*-[Pt(PEt₃)₂Cl₂] = $-(644 \pm 7)$; *trans*-[Pt(PPrⁱ)₂Cl₂] = $-(785 \pm 7)$; *trans*-[Pt{P(C₆H₁₁)₃}₂Cl₂] = $-(999 \pm 8)$; *cis*-[Pd(PPh₃)₂Cl₂] = 205 ± 10 ; *cis*-[Pt(PPh₃)₂Cl₂] = 173 ± 6 ; *cis*-[Pt(PMe₂Ph)₂Cl₂] = $-(280 \pm 5)$; *cis*[Pd(cod)Cl₂] = $-(234 \pm 1)$ -(cod = cyclo-octa-1,5-diene); *cis*-[Pt(cod)Cl₂] = $-(241 \pm 9)$; *cis*-[Pt(PEt₃)₂Me₂] = $-(520 \pm 6)$; *cis*-[Pt(PEt₃)₂(C₆H₄Me-o)₂] = $-(329 \pm 24)$; *cis*-[Pt(PEt₃)₂(CH₃)Cl] = $-(569 \pm 5)$; *cis*-[Pt(PEt₃)₂(C₆H₄Me-o)Cl] = $-(495 \pm 15)$; *cis*-[Pt(PEt₃)₂(SEt)₂] = $-(651 \pm 9)$; *cis*-[Pt(PPh₃)₂(SEt)₂] = 182 ± 14 ; *cis*-[Pd(MeCN)₂Cl₂] = $-(149 \pm 3)$; [Pt(PEt₃)₂Cl₄] = $-(863 \pm 7)$. 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 ΔH_f° for the gaseous complexes have served to derive bond-enthalpy contributions of L \rightarrow Pt and Pt-X bonds in [PtL₂X₂] compounds. The ligand bonding power to PtCl₂ decreases along the series PPrⁱ > P(C₆H₁₁)₃ > PEt₃ > PPh₃ > olefin (in cyclo-octa-1,5-diene). Bond-enthalpy contributions of Pt-X [relative to $E(\text{Pt-Cl}) = 290 \text{ kJ mol}^{-1}$] decrease in the series Pt-C* \sim Pt-Cl > Pt-C > Pt-S, where C* and C are trigonal and tetrahedral carbon (in Ph-Pt and CH₃-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-workers¹⁻⁴ on [Pt(PEt₃)₂Ph₂], [Pt(PPh₃)₂(COPh)Cl], [Pt-(PPh₃)₂(C₂H₄)], and [Pd(CH₂CH=CH₂)Cl]₂. The present work reports on the application of the high-temperature microcalorimeter to thermal-decomposition studies⁵ on selected Pt and Pd complexes with phosphines (PR₃) 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, $\Delta H_f^\circ(g)$, of the gaseous complexes. These provide a basis for the evaluation of the bond-energy contributions of Pt-X and L \rightarrow Pt in [PtL₂X₂] molecules for various ligands, L, with X = Cl, CH₃, C₆H₄Me-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 ³¹P n.m.r. spectra.

Auxiliary Data.—The following auxiliary ΔH_f° values (kJ mol⁻¹) were used in the evaluation of the present experimental results (certain of the chosen values are based on estimates): PtCl₂(c) = $-(140.6 \pm 4)$; ¹² PdCl₂(c) = $-(163.2 \pm 8)$; ¹³ PMe₃(g) = $-(101 \pm 5)$; ¹⁴ PEt₃(g) \sim -108 [estimated value; a literature value,¹⁴ $\Delta H_f^\circ(g) \sim -49.6 \text{ kJ mol}^{-1}$, leads to a seemingly low bond energy $\bar{D}(\text{P-Et})$, relative to $\bar{D}(\text{P-Me})$ and $\bar{D}(\text{P-Ph})$. From plots of $\bar{D}(\text{M-R})$ (M = N, P, As, Sb, or Bi; R = Me, Et, or Ph) given by Pilcher and Skinner¹⁵ the estimated $\Delta H_f^\circ \sim -108 \text{ kJ mol}^{-1}$ is consistent

with the general trend]; PPh₃(g) = 314 ± 14 ; ¹⁴ PPrⁱ₃(g) \sim -148 (estimated from application of the Allen scheme, e.g. ref. 16); P(C₆H₁₁)₃(g) \sim -205 (estimated from application of the Allen scheme); P(Me₂Ph)₃(g) \sim 37 [estimated from $\frac{1}{3}\Delta H_f^\circ(\text{PMe}_3) + \frac{1}{3}\Delta H_f^\circ(\text{PPh}_3)$]; PCl₃(g) = $-(289.5 \pm 1)$; ¹⁷ MeCl(g) = $-(82.0 \pm 0.5)$; ¹⁴ EtCl(g) = $-(112.1 \pm 0.5)$; ¹⁴ PrⁱCl(g) = $-(145 \pm 0.6)$; ¹⁴ C₆H₁₁Cl(g) = $-(163.6 \pm 3.6)$; ¹⁴ PhCl(g) = 51.3 ± 0.7 ; ¹⁴ C₆H₅CH₂Cl(g) = 18.7 ± 3 ; ¹⁴ C₂H₆(g) = $-(84.0 \pm 0.2)$; ¹⁴ C₁₄H₁₄(g) = 143 ± 1.8 ; ¹⁴ cyclo-C₈H₁₂(g) = 58.6 ± 1.2 ; ¹⁴ cyclo-C₈H₁₂Cl₂(g) \sim -121 (estimated, assuming ΔH for addition of Cl₂ to cod is of similar magnitude to ΔH for addition to C₂H₄); SEt₂(g) = $-(83.5 \pm 0.8)$; ¹⁴ P(S)Et₃(g) \sim -218 (estimated¹⁸); P(S)Ph₃(g) \sim 204 (estimated¹⁸); MeCN(g) = 74.0 ± 0.4 .¹⁹

Measured ΔH_f° 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.

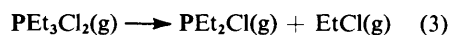
Results

cis-Dichlorobis(triethylphosphine)platinum(II), [Pt(PEt₃)₂Cl₂].—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(PEt₃)₂Cl₂]

Sample mass (mg)	Method	T/K	ΔH_{sub}^T kJ mol ⁻¹	$\Delta H_{\text{sub}}^{298}$ 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			
			ΔH^{603}	$\Delta H^{*,603}$	$\Delta H^{*,298}$		
			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			
$\Delta H_r^\circ[\text{Pt}(\text{PEt}_3)_2\text{Cl}_2, \text{cis}, \text{c}] = -(655 \pm 15) \text{ kJ mol}^{-1}$							
$\Delta H_r^\circ[\text{Pt}(\text{PEt}_3)_2\text{Cl}_2, \text{cis}, \text{g}] = -(481.6 \pm 21) \text{ kJ mol}^{-1}$							

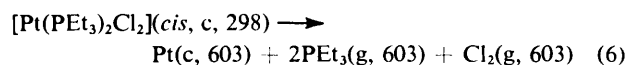
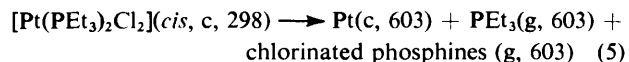


was formed on condensation of the hot vapours escaping from the reaction vessel (*e.g.* PEt₃Cl from EtCl and excess PEt₃). We cannot accurately assess the contribution to the measured heat of reaction from the chlorination reactions, as ΔH_r° values are not available for chlorinated phosphines. For complete chlorination [equation (4)], ΔH_r at 298 K is ~



-517 kJ mol⁻¹, and is virtually the same at *ca.* 600 K. We have assumed that for the partial chlorination [PEt₃(g) + Cl₂(g) → products (g)], the reaction heat is one-third of that for complete reaction, $\Delta H_r \sim -172 \text{ kJ mol}^{-1}$.

The measured ΔH^{603} (Table 1), relating to the cell reaction of equation (5) coupled with $\Delta H_r \sim -172 \text{ kJ mol}^{-1}$ for partial chlorination, yields $\Delta H^{*,603} = \Delta H^{603} + 172 \text{ (kJ mol}^{-1}\text{)}$ for the formal decomposition [equation (6)], from which $\Delta H^{*,298}$ and $\Delta H_r^\circ[\text{Pt}(\text{PEt}_3)_2\text{Cl}_2, \text{cis}, \text{c}]$ were derived.



trans-Dichlorobis(triethylphosphine)platinum(II), [Pt(PEt₃)₂Cl₂].—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.

trans-Dichlorobis(tri-isopropylphosphine)platinum(II), [Pt(PPr₃)₂Cl₂].—The vacuum-sublimation microcalorimetric

Table 2. Sublimation and thermal decomposition of *trans*-[Pt(PEt₃)₂Cl₂]

Sample mass (mg)	Method	T/K	ΔH_{sub}^T kJ mol ⁻¹	$\Delta H_{\text{sub}}^{298}$ 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			
			ΔH^{603}	$\Delta H^{*,603}$	$\Delta H^{*,298}$		
			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			
$\Delta H_r^\circ[\text{Pt}(\text{PEt}_3)_2\text{Cl}_2, \text{trans}, \text{c}] = -(643.6 \pm 7) \text{ kJ mol}^{-1}$							
$\Delta H_r^\circ[\text{Pt}(\text{PEt}_3)_2\text{Cl}_2, \text{trans}, \text{g}] = -(494.7 \pm 8) \text{ kJ mol}^{-1}$							

Table 3. Sublimation and thermal decomposition of *trans*-[Pt(PPr₃)₂Cl₂]

Sample mass (mg)	T/K	Method	ΔH_{sub}^T kJ mol ⁻¹	$\Delta H_{\text{sub}}^{298}$ 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			
			ΔH^T	$\Delta H^{*,T}$	$\Delta H^{*,298}$		
			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			
$\Delta H_r^\circ[\text{Pt}(\text{PPr}_3)_2\text{Cl}_2, \text{trans}, \text{c}] = -(785 \pm 7) \text{ kJ mol}^{-1}$							
$\Delta H_r^\circ[\text{Pt}(\text{PPr}_3)_2\text{Cl}_2, \text{trans}, \text{g}] = -(592 \pm 8) \text{ kJ mol}^{-1}$							

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(PEt₃)₂Cl₂]; the chlorination reaction [equation (7)] is calculated to have



$\Delta H_r \sim -576 \text{ kJ mol}^{-1}$ at 298 K, corresponding to a contribution from partial chlorination of liberated PPr₃ in the thermal-decomposition reaction of *ca.* -192 kJ mol⁻¹ at

Table 4. Thermal decomposition of *trans*-[Pt{P(C₆H₁₁)₃}₂Cl₂]

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

$$\Delta H_r^\circ[\text{Pt}\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2\text{Cl}_2, \text{trans}, \text{c}] = -(999.5 \pm 8) \text{ kJ mol}^{-1}$$

Table 5. Thermal decomposition of *cis*-[Pd(PPh₃)₂Cl₂]

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

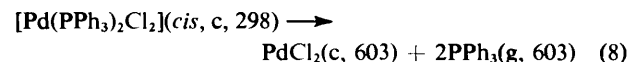
Mean
259.9 ± 10

$$\Delta H_r^\circ[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2, \text{cis}, \text{c}] = 205.3 \pm 10 \text{ kJ mol}^{-1}$$

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(C₆H₁₁)₃}₂Cl₂].—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(PEt₃)₂Cl₂]; in this case the complete chlorination reaction to form PCl₃(g) and chlorocyclohexane has $\Delta H_r \sim 575 \text{ kJ mol}^{-1}$ at 298 K, reducing to $\sim 573 \text{ kJ mol}^{-1}$ at temperatures near 600 K. The chlorination contribution to ΔH^T , taken as one third of this, is $\sim -191 \text{ kJ mol}^{-1}$.

cis-Dichlorobis(triphenylphosphine)palladium(II), [Pd(PPh₃)₂Cl₂].—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).



cis-Dichlorobis(triphenylphosphine)platinum(II), [Pt(PPh₃)₂Cl₂].—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)



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

Table 6. Thermal decomposition of *cis*-[Pt(PPh₃)₂Cl₂]

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

$$\Delta H_r^\circ[\text{Pt}(\text{PPh}_3)_2\text{Cl}_2, \text{cis}, \text{c}] = 173 \pm 6 \text{ kJ mol}^{-1}$$

Table 7. Thermal decomposition of *cis*-[Pt(PMe₂Ph)₂Cl₂]

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

$$\Delta H_r^\circ[\text{Pt}(\text{PMe}_2\text{Ph})_2\text{Cl}_2, \text{cis}, \text{c}] = -(280 \pm 5) \text{ kJ mol}^{-1}$$

Table 8. Thermal decomposition of *cis*-[Pd(cod)Cl₂]

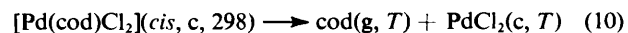
Sample mass (mg)	T/K	ΔH^T kJ mol ⁻¹	ΔH^{298} kJ mol ⁻¹
2.954	473	171.9	128.1
2.582	473	172.4	128.6
3.256	532	192.2	130.6
3.105	532	191.8	130.2
2.938	532	192.1	130.5
2.632	532	191.1	129.5
3.055	532	192.5	130.9

Mean
129.8 ± 0.8

$$\Delta H_r^\circ[\text{Pd}(\text{cod})\text{Cl}_2, \text{cis}, \text{c}] = -(234.4 \pm 1) \text{ kJ mol}^{-1}$$

cis-Dichlorobis(dimethylphenylphosphine)platinum(II), [Pt(PMe₂Ph)₂Cl₂].—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 $\text{PMe}_2\text{Ph} + 3\text{Cl}_2 \longrightarrow \text{PhCl} + 2\text{MeCl} + \text{PCl}_3$, $\Delta H_r \sim -439.2 \text{ kJ mol}^{-1}$ at 298 K. Allowing $\Delta H_r/3$ for the chlorination $\text{PMe}_2\text{Ph} + \text{Cl}_2 \longrightarrow$ products in the hot zone, the correction is $\sim -147 \text{ kJ mol}^{-1}$ at temperature $T \sim 600 \text{ K}$. Results are summarised in Table 7.

cis-Dichloro(cyclo-octa-1,5-diene)palladium(II), [Pd(cod)Cl₂].—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).



cis-Dichloro(cyclo-octa-1,5-diene)platinum(II), [Pt(cod)Cl₂].—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)Cl₂]

Sample mass (mg)	<i>T</i> /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

$$\Delta H_f^\circ[\text{Pt}(\text{cod})\text{Cl}_2, \text{cis}, \text{c}] = -(240.8 \pm 9) \text{ kJ mol}^{-1}$$

Table 10. Sublimation and thermal decomposition of *cis*-[Pt-(PEt₃)₂Me₂]

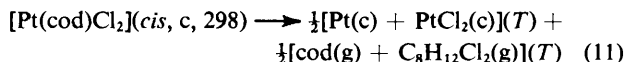
Sample mass (mg)	Method	<i>T</i> /K	ΔH^T kJ mol ⁻¹	ΔH^{298} kJ mol ⁻¹
2.132	v.s.	403	174.5	127.0
2.285	v.s.	403	184.0	136.5
2.116	v.s.	443	198.6	129.2
Mean $\Delta H_{\text{sub}}^{298} = 130.9 \pm 6 \text{ kJ mol}^{-1}$				
2.257	t.d.	573	368.2	221.5
2.093	t.d.	573	364.1	217.4
2.312	t.d.	573	380.4	233.7
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 $\Delta H^{298} = 220.3 \pm 6 \text{ kJ mol}^{-1}$

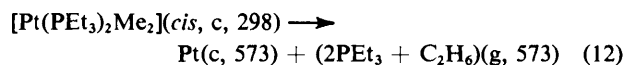
$$\Delta H_f^\circ[\text{Pt}(\text{PEt}_3)_2\text{Me}_2, \text{cis}, \text{c}] = -(520 \pm 6) \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ[\text{Pt}(\text{PEt}_3)_2\text{Me}_2, \text{cis}, \text{g}] = -(389 \pm 8) \text{ kJ mol}^{-1}$$

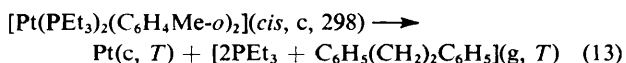
clean. The measured ΔH^T (Table 9) are related to the presumed decomposition reaction of equation (11).



cis-Dimethylbis(triethylphosphine)platinum(II), [Pt(PEt₃)₂Me₂].—Sublimation and thermal-decomposition results are summarized in Table 10. The ΔH^T values are related to the presumed hot-zone decomposition [equation (12)].



cis-Bis(*o*-tolyl)bis(triethylphosphine)platinum(II), [Pt(PEt₃)₂(C₆H₄Me-*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)].



cis-Chloro(methyl)bis(triethylphosphine)platinum(II), [Pt(PEt₃)₂(CH₃)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-(PEt₃)₂(C₆H₄Me-*o*)₂]

Sample mass (mg)	Method	<i>T</i> /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 $\Delta H_{\text{sub}}^{298} = 183.2 \pm 4 \text{ kJ mol}^{-1}$

$$2.001 \quad \text{t.d.} \quad 623 \quad 511.0 \quad 254.3$$

$$1.693 \quad \text{t.d.} \quad 623 \quad 492.6 \quad 235.9$$

$$2.063 \quad \text{t.d.} \quad 623 \quad 535.0 \quad 278.3$$

Mean $\Delta H^{298} = 256.2 \pm 24 \text{ kJ mol}^{-1}$

$$\Delta H_f^\circ[\text{Pt}(\text{PEt}_3)_2(\text{C}_6\text{H}_4\text{Me-}o)_2, \text{cis}, \text{c}] = -(329 \pm 24) \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ[\text{Pt}(\text{PEt}_3)_2(\text{C}_6\text{H}_4\text{Me-}o)_2, \text{cis}, \text{g}] = -(146 \pm 24) \text{ kJ mol}^{-1}$$

Table 12. Thermal decomposition of *cis*-[Pt(PEt₃)₂(CH₃)Cl]

Sample mass (mg)	<i>T</i> /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

$$\Delta H_f^\circ[\text{Pt}(\text{PEt}_3)_2(\text{CH}_3)\text{Cl}, \text{cis}, \text{c}] = -(569 \pm 5) \text{ kJ mol}^{-1}$$

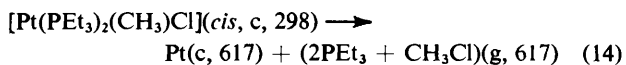
Table 13. Thermal decomposition of *cis*-[Pt(PEt₃)₂(C₆H₄Me-*o*)Cl]

Sample mass (mg)	<i>T</i> /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

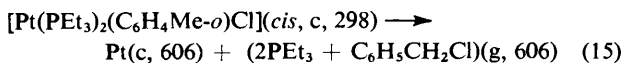
Mean
297.7 ± 15

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

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



cis-Chloro(*o*-tolyl)bis(triethylphosphine)platinum(II), [Pt(PEt₃)₂(C₆H₄Me-*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)].



cis-Bis(ethylthio)bis(triethylphosphine)platinum(II), [Pt(PEt₃)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

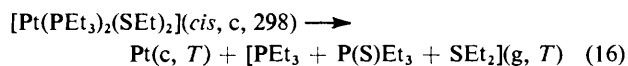
Table 14. Sublimation and thermal decomposition of *cis*-[Pt(PEt₃)₂(SEt)₂]

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 $\Delta H_{\text{sub}}^{298} = 195.7 \pm 11$ 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 $\Delta H^{298} = 241.0 \pm 9$ kJ mol ⁻¹				
$\Delta H_f^\circ[\text{Pt}(\text{PEt}_3)_2(\text{SEt})_2, \text{cis}, \text{c}] = -(650.5 \pm 9)$ kJ mol ⁻¹				
$\Delta H_f^\circ[\text{Pt}(\text{PEt}_3)_2(\text{SEt})_2, \text{cis}, \text{g}] = -(455 \pm 14)$ kJ mol ⁻¹				

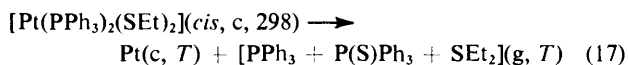
Table 15. Thermal decomposition of *cis*-[Pt(PPh₃)₂(SEt)₂]

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 \pm 14			
$\Delta H_f^\circ[\text{Pt}(\text{PPh}_3)_2(\text{SEt})_2, \text{cis}, \text{c}] = 181.6 \pm 14$ kJ mol ⁻¹			

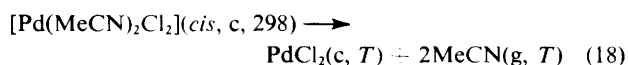
in the exit-tube. Results are interpreted in terms of the presumed hot-zone reaction [equation (16)].



cis-Bis(ethylthio)bis(triphenylphosphine)platinum(II), [Pt(PPh₃)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(PEt₃)₂(SEt)₂], presuming that liberated PPh₃ abstracts sulphur from the SEt fragments to form P(S)Ph₃ [equation (17)].



cis-Dichlorobis(methyl cyanide)palladium(II), [Pd(MeCN)₂-Cl₂].—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)].



cis-Tetrachlorobis(triethylphosphine)platinum(IV), [Pt(PEt₃)₂-Cl₄].—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

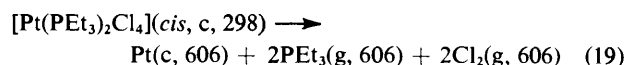
Table 16. Thermal decomposition of *cis*-[Pd(MeCN)₂Cl₂]

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 \pm 3			
$\Delta H_f^\circ[\text{Pd}(\text{MeCN})_2\text{Cl}_2, \text{cis}, \text{c}] = -(148.8 \pm 3)$ kJ mol ⁻¹			

Table 17. Thermal decomposition of *cis*-[Pt(PEt₃)₂Cl₄]

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 \pm 7				
$\Delta H_f^\circ[\text{Pt}(\text{PEt}_3)_2\text{Cl}_4, \text{cis}, \text{c}] = -(863 \pm 7)$ kJ mol ⁻¹				

liquid in the cooler exit-tube. The measured ΔH^{606} (Table 17) include the contribution from chlorination of liberated PEt₃, for which correction is made as in the case of [Pt(PEt₃)₂Cl₂], to give $\Delta H^{*,606}$ for the decomposition [equation (19)].



Discussion

The collected results of the present studies are summarized in Table 18, which lists values for $\Delta H_f^\circ(\text{c})$, $\Delta H_{\text{sub}}^\circ$, and $\Delta H_f^\circ(\text{g})$ 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(PEt₃)₂-Me₂] and [Pt(PEt₃)₂(C₆H₄Me-*o*)₂] served to draw a parallel line through the point for *cis*-[Pt(PEt₃)₂Cl₂] which was used to obtain values for *cis*-[PtL₂Cl₂] compounds. A line through *trans*-[Pt(PEt₃)₂Cl₂] and *trans*-[Pt(PPR¹)₃Cl₂] was extended to obtain ΔH_{sub} for *trans*-[Pt{P(C₆H₁₁)₃}₂Cl₂]. The values accepted for the complexes of PdCl₂ are probably less reliable; available experimental data indicate that ΔH_{sub} for PdCl₂ is larger than that for PtCl₂ by ca. 40 kJ mol⁻¹. We have presumed that the sublimation heats of [PdL₂Cl₂] may be higher than those of the corresponding [PtL₂Cl₂] by 10 kJ mol⁻¹.

The uncertainty attached to each $\Delta H_f^\circ(\text{g})$ 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, $\Delta H_D(\text{g})$, for complexes containing PtCl₂ or PdCl₂, and values of ΔH_{diss} for all complexes. The enthalpies of ligand disruption, $\Delta H_D(\text{g})$, refer to equation (20a) or (20b), accepting available

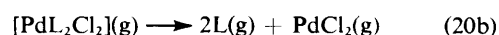
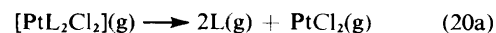


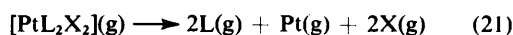
Table 18. Collected values of $\Delta H_f^\circ(\text{c})$, $\Delta H_{\text{sub}}^\circ$, and $\Delta H_f^\circ(\text{g})$

Compound	$\frac{\Delta H_f^\circ(\text{c})}{\text{kJ mol}^{-1}}$	$\frac{\Delta H_{\text{sub}}^\circ}{\text{kJ mol}^{-1}}$	$\frac{\Delta H_f^\circ(\text{g})}{\text{kJ mol}^{-1}}$
<i>cis</i> -[Pt(PEt ₃) ₂ Cl ₂]	-(655 ± 15)	174 ± 16	-(482 ± 21)
<i>trans</i> -[Pt(PEt ₃) ₂ Cl ₂]	-(644 ± 7)	149 ± 3	-(495 ± 8)
<i>trans</i> -[Pt(PPr ¹) ₂ Cl ₂]	-(785 ± 7)	193 ± 4	-(592 ± 8)
<i>trans</i> -[Pt{P(C ₆ H ₁₁) ₃ } ₂ Cl ₂]	-(999 ± 8)	300 *	-(699 ± 21)
<i>cis</i> -[Pd(PPh ₃) ₂ Cl ₂]	205 ± 10	285 *	490 ± 22
<i>cis</i> -[Pt(PPh ₃) ₂ Cl ₂]	173 ± 6	275 *	448 ± 21
<i>cis</i> -[Pt(PMe ₂ Ph) ₂ Cl ₂]	-(280 ± 5)	185 *	-(95 ± 21)
<i>cis</i> -[Pd(cod)Cl ₂]	-(234 ± 1)	140 *	-(96 ± 20)
<i>cis</i> -[Pt(cod)Cl ₂]	-(241 ± 9)	130 *	-(111 ± 22)
<i>cis</i> -[Pt(PEt ₃) ₂ Me ₂]	-(520 ± 6)	131 ± 6	-(389 ± 8)
<i>cis</i> -[Pt(PEt ₃) ₂ (C ₆ H ₄ Me- <i>o</i>) ₂]	-(329 ± 24)	183 ± 4	-(146 ± 24)
<i>cis</i> -[Pt(PEt ₃) ₂ (CH ₃)Cl]	-(569 ± 5)	152 *	-(417 ± 21)
<i>cis</i> -[Pt(PEt ₃) ₂ (C ₆ H ₄ Me- <i>o</i>)Cl]	-(495 ± 15)	179 *	-(316 ± 25)
<i>cis</i> -[Pt(PEt ₃) ₂ (SEt) ₂]	-(651 ± 9)	196 ± 11	-(455 ± 14)
<i>cis</i> -[Pt(PPh ₃) ₂ (SEt) ₂]	182 ± 14	295 *	477 ± 25
<i>cis</i> -[Pd(MeCN) ₂ Cl ₂]	-(149 ± 3)	132 *	-(17 ± 20)
<i>cis</i> -[Pt(PEt ₃) ₂ Cl ₄]	-(863 ± 7)	200 *	-(663 ± 21)

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

Compound	$\frac{\Delta H_D^\circ(\text{g})}{\text{kJ mol}^{-1}}$	$\frac{\Delta H_{\text{diss}}^\circ}{\text{kJ mol}^{-1}}$
<i>cis</i> -[Pt(PEt ₃) ₂ Cl ₂]	376 ± 21	1 073 ± 21
<i>trans</i> -[Pt(PEt ₃) ₂ Cl ₂]	390 ± 8	1 087 ± 8
<i>cis</i> -[Pt(PEt ₃) ₂ (CH ₃)Cl]		1 032 ± 21
<i>cis</i> -[Pt(PEt ₃) ₂ Me ₂]		1 027 ± 10
<i>cis</i> -[Pt(PEt ₃) ₂ (C ₆ H ₄ Me- <i>o</i>)Cl]		1 086 ± 28
<i>cis</i> -[Pt(PEt ₃) ₂ (C ₆ H ₄ Me- <i>o</i>) ₂]		1 094 ± 29
<i>cis</i> -[Pt(PEt ₃) ₂ (SEt) ₂]		1 017 ± 20
<i>cis</i> -[Pt(PEt ₃) ₂ Cl ₄]		1 496 ± 21
<i>trans</i> -[Pt(PPr ¹) ₂ Cl ₂]	406 ± 8	1 104 ± 8
<i>trans</i> -[Pt{P(C ₆ H ₁₁) ₃ } ₂ Cl ₂]	399 ± 21	1 097 ± 21
<i>cis</i> -[Pt(PMe ₂ Ph) ₂ Cl ₂]	279 ± 21	977 ± 21
<i>cis</i> -[Pt(PPh ₃) ₂ Cl ₂]	291 ± 21	986 ± 21
<i>cis</i> -[Pt(PPh ₃) ₂ (SEt) ₂]		929 ± 29
<i>cis</i> -[Pt(cod)Cl ₂]	280 ± 22	978 ± 22
<i>cis</i> -[Pd(cod)Cl ₂]	283 ± 20	769 ± 20
<i>cis</i> -[Pd(PPh ₃) ₂ Cl ₂]	266 ± 22	753 ± 22
<i>cis</i> -[Pd(MeCN) ₂ Cl ₂]	293 ± 20	780 ± 20

values,²² $\Delta H_f^\circ(\text{PtCl}_2, \text{g}) \sim 110.5 \text{ kJ mol}^{-1}$, and ¹³ $\Delta H_f^\circ(\text{PdCl}_2, \text{g}) \sim 128 \text{ kJ mol}^{-1}$. The enthalpies of dissociation $\Delta H_{\text{diss}}^\circ$ 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).



The $\Delta H_{\text{diss}}^\circ$ values were derived using the following $\Delta H_f^\circ(\text{g})$ 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 CH₃(g) = 144 ± 3;²⁴ C₆H₄Me-*o*(g) = 299 ± 12 [estimated assuming $D(\text{H}-\text{C}_6\text{H}_4\text{Me}) = D(\text{H}-\text{C}_6\text{H}_5)$];²⁵ SEt(g) = 106 ± 10.²⁶

The values $\Delta H_D^\circ/2$ provide a measure of the bonding power of the various donor ligands to PtCl₂ or PdCl₂. These indicate decreasing ligand bonding power to PtCl₂ in the sequence PPr¹ > P(C₆H₁₁)₃ > PEt₃ > PPh₃ > PMe₂Ph ~ ½(cod).

From a previous study,⁵ we may add: ½(cod) > pyridine > NH₂Pr¹ > NH₂Me > NH₃. The few available data on [PdL₂Cl₂] complexes suggest that ligands bind to PdCl₂ with similar power as to PtCl₂.

The values $\Delta H_{\text{diss}}^\circ$ provide 'bond-enthalpy contributions' of the metal-ligand and metal-X bonds in a complex

[PtL₂X₂], on the basis of bond additivity [equation (22)].

$$\Delta H_{\text{diss}}^\circ[\text{PtL}_2\text{X}_2] = 2\bar{E}(\text{Pt}-\text{L}) + 2\bar{E}(\text{Pt}-\text{X}) \quad (22)$$

The analysis in Table 20 is derived from the acceptance of a constant transferable $\bar{E}(\text{Pt}-\text{Cl}) = 290 \text{ kJ mol}^{-1}$, which is less than the mean bond-dissociation enthalpy, $\bar{D}(\text{Pt}-\text{Cl}) = 349 \text{ kJ mol}^{-1}$ in gaseous PtCl₂, and in gaseous PtCl₃ (295 kJ mol⁻¹),²² but larger than in Pt₆Cl₁₂ (g), where $\bar{D}(\text{Pt}-\text{Cl}) \sim 229 \text{ kJ mol}^{-1}$.²⁷ {The crystal-structure analysis of discrete Pt₆Cl₁₂ groups in PtCl₂ by Brodersen *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(PEt₃)₂Cl₂], where Messmer and Amma²⁹ found Pt-Cl ~ 2.29 Å. Bond lengths in the gaseous molecules PtCl₂, PtCl₃, and PtCl₄ have not been measured.}

The choice $\bar{E}(\text{Pd}-\text{Cl}) \sim 215 \text{ kJ mol}^{-1}$ is also less than $\bar{D}(\text{Pd}-\text{Cl}) \sim 243 \text{ kJ mol}^{-1}$ in PdCl₂(g), and larger than in Pd₅Cl₁₀(g), where $\bar{D} \sim 182 \text{ kJ mol}^{-1}$.²⁶

The main conclusions drawn from Table 20 are as follows. (i) The trialkylphosphine ligands bind more firmly to PtCl₂ 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(PEt₃)₂Cl₂] relative to the single bond length (2.41 Å) also indicates some double-bond character, Pt ↔ P. (ii) The contribution $\bar{E}(\text{PPh}_3 \rightarrow \text{Pt})$ is less than for alkylphosphine ligands, and steric crowding may be a contributory factor. The lower value for $\bar{E}(\text{PMe}_2\text{Ph} \rightarrow \text{Pt})$, however, suggests that the phenyl group attached to P is the main cause of reduced ligand power. (iii) The contribution $\bar{E}(\text{||} \rightarrow \text{Pt})$ from cod, of similar magnitude to $\bar{E}(\text{PPh}_3 \rightarrow \text{Pt})$, 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 $\bar{E}(\text{||} \rightarrow \text{Pt})$ from ethylene in [Pt(PPh₃)₂(C₂H₄)] is likewise influenced, probably more so, by reorganization of the ethylene ligand on dissociation. (The C=C bond in the complex³¹ is *ca.* 0.09 Å longer than in free ethylene.) The contribution $\bar{E}(\text{|||} \rightarrow \text{Pt})$ from diphenylacetylene in [Pt(PPh₃)₂(PhC≡CPh)] includes a reorganization energy of the formal C≡C bond, which is longer in the analogous [Pt(PhC≡CPh)₂] complex³² by *ca.* 0.08 Å than in the free

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

Basis	Compound	Derived $\bar{E}(L \rightarrow Pt)$	
$\bar{E}(Pt-Cl) = 290$	<i>trans</i> -[Pt(PPt ¹) ₂ Cl ₂]	PPt ¹ \rightarrow Pt = 262 \pm 4	
	<i>trans</i> -[Pt{P(C ₆ H ₁₁) ₃ }Cl ₂]	P(C ₆ H ₁₁) ₃ \rightarrow Pt = 258.5 \pm 10	
	<i>trans</i> -[Pt(PEt ₃) ₂ Cl ₂]	PEt ₃ \rightarrow Pt = 253.5 \pm 4	
	<i>cis</i> -[Pt(PEt ₃) ₂ Cl ₂]	PEt ₃ \rightarrow Pt = 246.5 \pm 10	
	<i>cis</i> -[Pt(PPh ₃) ₂ Cl ₂]	PPh ₃ \rightarrow Pt = 203 \pm 10	
	<i>cis</i> -[P(PMe ₂ Ph) ₂ Cl ₂]	PMe ₂ Ph \rightarrow Pt = 199 \pm 10	
	[Pt(cod)Cl ₂]	\rightarrow Pt = 199 \pm 11	
	<i>cis</i> -[Pt(NC ₅ H ₅) ₂ Cl ₂]	NC ₅ H ₅ \rightarrow Pt \sim 181 \pm 8	
	<i>cis</i> -[Pt(NH ₂ Pr ¹) ₂ Cl ₂]	NH ₂ Pr ¹ \rightarrow Pt \sim 177 \pm 8	
	<i>cis</i> -[Pt(NH ₂ Me) ₂ Cl ₂]	NH ₂ Me \rightarrow Pt \sim 167 \pm 8	
	<i>cis</i> -[Pt(NH ₃) ₂ Cl ₂]	NH ₃ \rightarrow Pt \sim 156 \pm 8	
	$\bar{E}(PEt_3 \rightarrow Pt) = 246.5$	<i>cis</i> -[Pt(PEt ₃) ₂ Me ₂]	Pt-CH ₃ = 267 \pm 5
		<i>cis</i> -[Pt(PEt ₃) ₂ (C ₆ H ₄ Me- <i>o</i>) ₂]	Pt-C ₆ H ₄ Me- <i>o</i> = 300 \pm 15
<i>cis</i> -[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 ₆ H ₄ Me- <i>o</i>)Cl]		Pt-C ₆ H ₄ Me- <i>o</i> = 303 \pm 14	
$\bar{E}(PPh_3 \rightarrow Pt) = 203$	<i>cis</i> -[Pt(PPh ₃) ₂ (SEt) ₂]	Pt-SEt = 262 \pm 15	
	[Pt(PPh ₃) ₂ (PhC \equiv CPh)] ^a	\rightarrow Pt = 182 \pm 26	
	[Pt(PPh ₃) ₂ (CH ₂ =CH ₂)] ^b	\rightarrow Pt = 154 \pm 28	
$\bar{E}(Pd-Cl) = 215$	<i>cis</i> -[Pd(MeCN) ₂ Cl ₂]	MeCN \rightarrow Pd = 175 \pm 10	
	<i>cis</i> -[Pd(cod)Cl ₂]	\rightarrow Pd = 169 \pm 10	
	<i>cis</i> -[Pd(PPh ₃) ₂ Cl ₂]	PPh ₃ \rightarrow Pd = 162 \pm 10	
$\bar{E}(PEt_3 \rightarrow Pt) = 246.5$ or $\bar{E}(Pt-Cl) = 290$	[Pt(PEt ₃) ₂ Cl ₄]	Pt-Cl = 125 \pm 5	
		PEt ₃ \rightarrow 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 $\Delta H_f^\circ[\text{Pt}(\text{PPh}_3)_2\text{Cl}_2, \text{c}]$ gives $\Delta H_f^\circ(\text{c}) = 731.5 \pm 16$ kJ mol⁻¹. We have estimated $\Delta H_{\text{sub}} \sim 285 \pm 20$ kJ mol⁻¹, to obtain $\Delta H_f^\circ(\text{g}) = 1016.5 \pm 26$ and $\Delta H_{\text{diss}} = 588 \pm 26$ kJ mol⁻¹. ^b A. Evans, C. T. Mortimer, and R. J. Puddephat, *J. Organomet. Chem.*, 1975, **85**, 101; coupled with $\Delta H_f^\circ[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{Ph}_2)]$ from the reference in footnote *a* and our estimate, $\Delta H_{\text{sub}} \sim 230 \pm 20$ kJ mol⁻¹, to obtain $\Delta H_f^\circ(\text{g}) = 686 \pm 28$ and $\Delta H_{\text{diss}} = 560 \pm 28$ kJ mol⁻¹.

ligand. These CC bond length changes alone correspond to reorganization energies of the order ³³ 50 (cod), 110 (C₆H₄), 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 ||| \rightarrow Pt > || \rightarrow Pt > | (in cod) \rightarrow 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-C₆H₄Me-*o*) is larger than for attachment to -CH₃; the difference reflects that between the bond dissociation enthalpies, $D(\text{Ph-H}) - D(\text{CH}_3\text{-H}) \sim 30$ 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(PEt₃)₂Cl₄], retention of the $\bar{E}(PEt_3 \rightarrow Pt)$ value requires a reduced value for $\bar{E}(Pt-Cl)$, and *vice versa*. (vii) The values $\bar{E}(PPh_3 \rightarrow Pd)$ and $\bar{E}(| \rightarrow Pd)$ are lower by 30-40 kJ mol⁻¹ than the corresponding \bar{E} values to Pt; $\bar{E}(\text{MeCN} \rightarrow Pd)$ is slightly less than $\bar{E}(\text{NC}_5\text{H}_5 \rightarrow Pt)$; data on MeCN \rightarrow Pt complexes are not available for direct comparison.

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