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THERMOCHEMISTRY OF THE OXIDATIVE ADDITION REACTION

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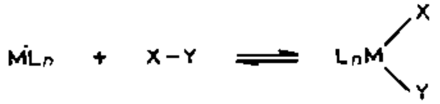
CONTENTS

A. INTRODUCTION

The major goal of this review is to bring together the information obtained to date on the thermochemistry of the oxidative addition reaction and related processes. Having done so, general trends and features will be discussed for those systems where sufficient data have been obtained under comparable conditions.

The oxidative addition reaction has been the subject of a great deal of work since the early reports of Vaska on addition of small molecules to square-planar iridium(I) compounds [1,2]. This is due to the synthetic utility of the reaction [3] and its occurrence in most types of homogeneous catalytic systems involving transition metal complexes in reactions of organic compounds [2–6]. Definitions of the reaction have been prepared by Collman and Roper [3] and Tolman [6]. In the reaction



$$ML_n + X{-}Y \rightleftharpoons L_nM(X)(Y) \qquad (1)$$

the oxidation state, coordination number and effective atomic number

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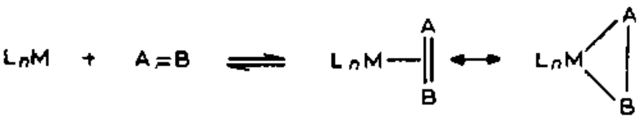
increase by two. This is a thermodynamic rather than mechanistic definition, relating products and starting materials.

The classification includes reactions which have been proposed to proceed by stepwise mechanisms (CH_3I + *trans*-[IrCl(CO)(PPh_3)$_3$] [7,8]), concerted (H_2 + *trans*-[IrCl(CO)(PPh_3)$_2$] [7]) or free radical mechanisms ($CH_3CHBrCO_2Et$ + *trans*-[IrCl(CO)(PMe_3)$_2$] [9]). As the term is generally used it also includes addition of unsaturated molecules in which the added molecule is not cleaved into two ligand moieties. Examples of this type are the reactions of dioxygen, olefins, acetylenes and other unsaturated molecules with low-valent metal centers [2–4]:



(2)

The relative importance of the two resonance structures as a function of the nature of A=B has been widely discussed [10].

The thermochemistry of these reactions provides an important insight into the activation of small molecules by metal complexes. The X–Y bond is replaced by the M—X and M—Y bonds which are usually weaker than the original bond or in the case of an unsaturated molecule, A=B, the bond order in the unsaturated molecule may be reduced [10]. The free energy change is the measure of the stability of the adducts relative to starting materials but the enthalpy change is a more direct look at the activation of the addend molecule. It is primarily a reflection of the strength of bonds formed and broken but it may also include contributions from solvation effects for reactants and products.

Most thermochemical work has centered on reactions of complexes in which the metal has a d^8 or d^{10} electron configuration. Synthetic and structural aspects of oxidative addition chemistry have been extensively developed. Kinetic and mechanistic studies have been carried out on a fair number of model systems such as O_2 [7], H_2 [7], CH_3I [7,8] and $(NC)_2C{=}C(CN)_2$ [10,11]. The thermochemistry has been the least investigated aspect of this reaction type. This review will cover the work done on four-coordinate d^8 systems represented by square-planar complexes of cobalt, rhodium and iridium in the +1 oxidation state, platinum in the +2 oxidation state and d^{10}, platinum(0) compounds.

B. THERMOCHEMICAL SYSTEM

The complete thermochemical system for an oxidative addition reaction is given in Fig. 1. The terms used there are as follows: $\Delta H_{(\mathrm{soln})}$ = heat of

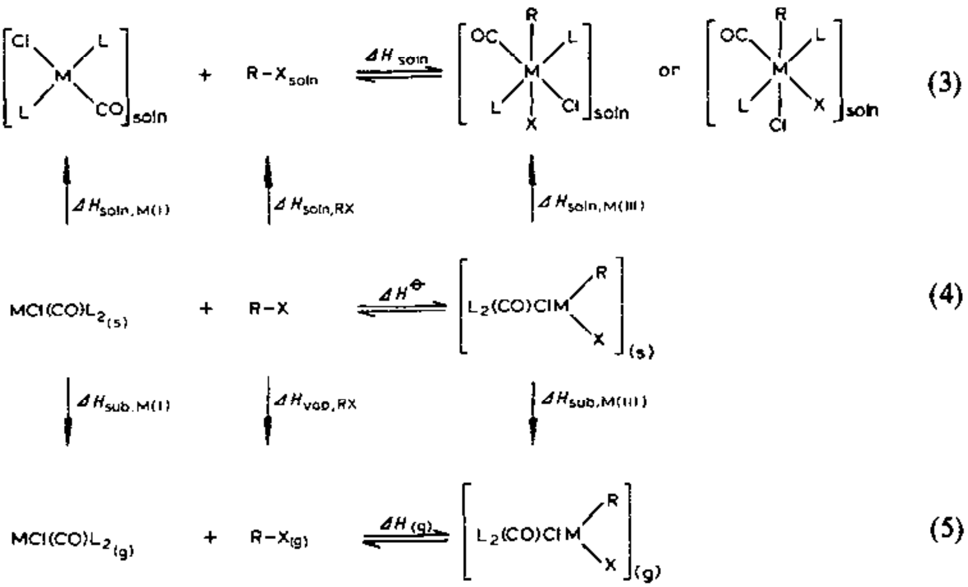


Fig. 1. Thermochemistry of the oxidative addition reaction.

reaction in homogeneous solution; $\Delta H^{\ominus}$ = standard heat of reaction, all reactants in their standard state; $\Delta H_{(gas)}$ = heat of reaction in the gas phase; $\Delta H_{soln,M(Z)}$ = heat of solution of reduced metal complex; $\Delta H_{soln,M(Z+2)}$ = heat of solution of oxidized metal complex; $\Delta H_{soln,addend}$ = heat of solution of addend; $\Delta H_{sub,M(Z)}$ = heat of sublimation of reduced metal complex; $\Delta H_{sub,M(Z+2)}$ = heat of sublimation of oxidized metal complex; $\Delta H_{vap,addend}$ = heat of vaporization of addend. This scheme refers to reactions in which no prior ligand dissociation from the reduced metal complex is involved in the reaction. Thus, it applies to the case of four-coordinate d^8 and two-coordinate d^{10} complexes. Five-coordinate d^8 and three- or four-coordinate d^{10} complexes would require additional terms for dissociation of one or two ligands from the reduced metal complex to provide coordination sites for the addend molecule in the oxidized product [3]. Most work to date has yielded $\Delta H_{(soln)}$ either from the temperature dependence of equilibrium constants or calorimetric measurements. The standard enthalpy change, $\Delta H^{\ominus}$, has been determined in relatively few cases. Usually this is accomplished by determining $\Delta H_{(soln)}$ and the appropriate heats of solution of reactants and products using

$$\Delta H^{\ominus} = \Delta H_{(soln)} - \Delta H_{soln,M(Z+2)} + \Delta \mathrm{H}_{soln,M(Z)} + \Delta \mathrm{H}_{soln,addend} \tag{6}$$

eqn. (6). The importance of $\Delta H^{\ominus}$ is that it can be combined with heats of formation of substances to calculate new data.

The value of the heat of reaction in the gas phase has rarely been determined. The necessary heats of sublimation are generally not measurable due to the low vapor pressure and/or low thermal stability of the compounds involved. In general, it has been the practice to assume, without evidence, that the heats of sublimation of reactant and product complexes are approximately the same which reduces eqn. (7) to eqn. (8).

$$\Delta H_{\text{gas}} = \Delta H^{\ominus} + \Delta H_{\text{sub,M}(Z+2)} - \Delta H_{\text{sub,M}(Z)} - \Delta H_{\text{vap,addend}} \tag{7}$$

$$\approx \Delta H^{\ominus} - \Delta H_{\text{vap,addend}} \tag{8}$$

The gas-phase data are directly relatable to the dissociation energies of the new metal–ligand bonds, eqn. (9).

$$\Delta H_{\text{gas}} = D(\text{X—Y}) - D(\text{M—X}) - D(\text{M—Y}) \tag{9}$$

In the case of addition of unsaturated molecules which remain intact upon coordination, the gas-phase ΔH is the negative of the metal–addend dissociation energy [eqn. (10)].

$$\Delta H_{\text{gas}} = -D(\text{M–addend}) \tag{10}$$

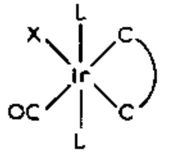
These data are rare for organometallic compounds so even approximated values have a place at present as long as the approximations are clearly indicated and recognized by those who use the data.

C. DATA

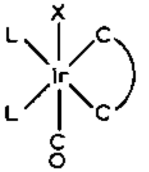
Thermodynamic data for reactions of cobalt(I), rhodium(I), iridium(I) and platinum(0 and II) are given in Tables 1–4. All values of ΔH from the literature have been converted to kJ mol^{-1} and in each case the method and solvent are given. In those cases where ΔH for the solution phase and standard state have been determined, both values are given. In many cases sufficient experimental detail is not available in the literature to assess uncertainties in the data so error limits, where given in the tables, are those reported in the original work.

Much of the data have been obtained using spectrophotometric methods to determine equilibrium constants, thence ΔH from the temperature dependence. Recently, more use of reaction and titration calorimetry has appeared. Differential scanning calorimetry has been applied to a few cases but is limited primarily to reactions in which the addend is irreversibly removed by heating solid complexes. Kinetic studies of forward and reverse reaction have also provided some thermodynamic data. Gas chromatography has also been used. The uses and limitations of these methods have been amply discussed in a recent review of thermodynamic data for olefin and acetylene complexes [12].

The addition of olefins to iridium complexes of the type *trans*-$[IrX(CO)L_2]$ ($X =$ anion and $L =$ tertiary phosphine) has been the subject of several studies [13–20]. The structure of the product has not in general been established unambiguously. The isomers possible where the addend functions as a bidentate ligand are given below. The structure of the tetracyanoethylene adduct of Vaska's complex ($X = Cl$ and $L = PPh_3$) has been



I



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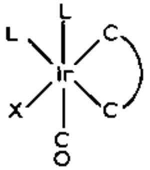
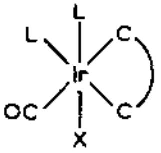


III



IV

determined by X-ray diffraction to be II [21] and is presumed to have the same geometry in solution. Other complexes of TCNE have tentatively been assumed to have the same geometry [17]. Geometry I has been tentatively assigned to the ethylene adduct of Vaska's complex and other complexes of olefins with substituents of low electronegativity [13]. Workers have used a number of different solvents so the work of different groups is not directly comparable. The effect of solvent on the enthalpy change has been determined for addition of TCNE to Vaska's complex. The reaction is more exothermic in 1,2-dichloroethane (-106.3 ± 2.5 kJ mol^{-1}) than in benzene (-83.3 ± 0.8 kJ mol^{-1}) [17]. This difference (23.0 ± 3.3 kJ mol^{-1}) was ascribed primarily to the heat of disruption of the benzene–TCNE complex which is known to be 15.1 ± 0.4 kJ mol^{-1} [22].

The solvent dependence of K for addition of TCNE to *trans*-$[RhCl(CO)(PPh_3)_2]$ has been found to vary and K decreases in the order benzonitrile > acetone > tetrahydrofuran [11].

Strohmeier and Fleischmann have investigated the effect of olefin, anion and phosphorus-donor ligand on ΔH and K for addition to iridium complexes [14], *trans*-$[IrX(CO)L_2]$. The trends in K paralleled those in ΔH. The dependence on ligand was the reaction becoming less exothermic in the order $P(OPh)_3 > PPh_3 > PCy_3$ and the trend for olefin was $OC(O)CH{=}CHC(O) < CH_2{=}CHCO_2Et <$ *cis*-$MeOC(O)CH{=}CHC(O)OMe <$ *trans*-$MeOC(O)CH{=}CHC(O)OMe$. No single trend as a function of anion, X, was observed. For maleic anhydride addition, $-\Delta H$ varied as $Cl < Br < I$ for $L = P(OPh)_3$ and $Cl > Br > I$ for $L = PPh_3$. For dimethylmaleate and $L = P(OPh)_3$ it was $Br > Cl > I$.

The dependence of ΔH (in C_6H_6) for addition of TCNE on the ligand L was investigated by Blake and co-workers. They found $-\Delta H$ varied as $PEt_3 > PMe_3 > PMe_2Ph > PEt_2Ph > PMePh_2 > P(OPh)_3 = P(CH_2Ph)_3 >$

TABLE 1

Thermochemical data for the reaction *trans*-$IrX(CO)L_2$ + addend ⇌ 1 : 1 complex

L	X	Addend	$-\Delta H$ (kJ mol^{-1})	K
PPh_3	Cl	$H_2C{=}CH_2$	49.4	1.1
	I		50.2	1.1
	I			2.7
	Cl	$H_2C{=}CH(CN)$		1.2
	I			0.4
	Cl	$(NC)HC{=}CH(CN)$		1.5×10^3
	I			87
$P(OPh)_3$	Cl	$OC(O)CH{=}CHCCO$	47.3	9.1×10^3
	Br		49.4	4.5×10^3
	I		54.8	2.1×10^3
PPh_3	Cl		44.8	3.6×10^3
	Br		35.6	1.9×10^3
	I		29.7	60
PCy_3	Cl		26.8	5
	Br		13.8	3
$P(OPh)_3$	Cl	*cis*-$CH_3OC(O)CH{=}CHC(O)OCH_3$	57.7	1×10^3
	Br		63.2	4×10^2
	I		53.6	1×10^2
PPh_3	Cl		48.1	5
	Br		50.2	2
	I		31.4	0.3
$P(OPh)_3$	Cl	*trans*-$CH_3OC(O)CH{=}CHC(O)OCH_3$	58.6	4.5
	Br		41.8	1.3
	Cl	$CH_2{=}CHCO_2C_2H_5$	49.0	38
	Br		47.7	22
	I		83.7	11
PPh_3	Cl		38.5	0.3
	Br		23.8	0.1
$P(OPh)_3$	Cl	$C_6H_5CH{=}CH_2$		2.7×10^{-2}
	Cl	n-$C_5H_{11}CH{=}CH_2$		0.1
PPh_3	Cl	$F_2C{=}CF_2$		>100
	F		79.4 ± 1.9	
	Cl		67.2 ± 1.9	
	Br		41.0 ± 0.7	
	I		57.2 ± 2.0	
PPh_3	Cl	$(NC)_2C{=}C(CN)_2$		1.4×10^5
			86.2 ± 0.8	
	F		100.0 ± 0.4	
	Cl		83.3 ± 0.8	
	Cl		106.3 ± 2.5	
	Br		77.8 ± 2.5	
	I		52.7 ± 2.9	
PMe_3	Cl	$(NC)_2C{=}C(CN)_2$	136.0 ± 0.8	

T (°C)	Solvent	Other	Method	Ref.
30	chlorobenzene	$\Delta S = -163.1\ \mathrm{J\ K^{-1}\ mol^{-1}}$	spectrophotometric	13
30	chlorobenzene			
20	chlorobenzene			
30	chlorobenzene			
30	toluene			
30	chlorobenzene			
20	toluene			14
30	chlorobenzene			13
207	solid		DSC	15
172,202				
162,197				
182,197				
30	tetrahydrofuran		spectrophotometric	13
—	benzene		calorimetry	16
25				17
	1,2-dichloroethane			
	benzene			
				18

TABLE 1 (continued)

L	X	Addend	$-\Delta H$ (kJ mol^{-1})	K
PMe_2Ph			118.4 ± 3.8	
$P(OPh)_3$			87.4 ± 4.1	
$PMePh_2$			104.6 ± 0.8	
PEt_3			146.4 ± 0.8	
PEt_2Ph			110.9 ± 0.8	
$P(Bu^t)Ph_2$			68.2 ± 2.9	
PCy_3			no reaction	
$AsPh_3$			82.4 ± 2.1	
PPh_3	Cl	$HC{\equiv}CH$	38.9	1.2
PPh_3	F	$CH_3O_2CC{\equiv}CCO_2CH_3$	52.7 ± 0.4	1320
	Cl		61.1 ± 0.4	840
PPh_3	Br		62.3 ± 1.2	$\sim 2 \times 10^4$
	I		64.4 ± 1.2	$> 10^5$
	NCS		33.5 ± 2.4	76
	N_3		52.7 ± 1.2	3.5×10^3
$PMePh_2$	Cl		62.8 ± 1.3	$> 10^4$
	Br		65.7 ± 0.8	$> 10^4$
$AsPh_3$	Cl		55.2 ± 0.4	$> 10^4$
PPh_3	F	$CF_3C{\equiv}CCF_3$	99.2 ± 0.3	
	Cl		95.7 ± 1.7	
	Br		78.6 ± 0.5	
	I		88.2 ± 3.2	
PPh_3	F	O_2		291
	Cl			7320
			71.5	1.71×10^4
			−92 ± 0.4	
			87.0	
	Br			6.2×10^4
	I			8.57×10^5
	NCO			331
	N_3			5600
$P(p\text{-Tol})_3$				2.1×10^4
$P(m\text{-Tol})_3$				7×10^3
$P(o\text{-Tol})_3$				no reaction
PCy_3				66
PPh_3	F	SO_2	53.6 ± 2.1	
	Cl		42.3	1320
			47.3	
			47.7 ± 2.5	
			−40 ± 1	
	Br		48.1 ± 2.5	
	I		34.7 ± 3.8	
PMe_2Ph	Cl		59.0 ± 10.9	
$P(OPh)_3$			no reaction	

T (°C)	Solvent	Other	Method	Ref.
				17
	1,2-dichloroethane			19
				20
	benzene			17
20	chlorobenzene		spectrophotometric	13
25	benzene		calorimetry	17
177	solid state		DSC	15
157				
177				
207				
40	benzene		spectrophotometric	29
	chlorobenzene			
30		$\Delta S = -154.8$ J K^{-1} mol^{-1}		13
25	solid state		DSC	31
	chlorobenzene		calorimetry	
40			spectrophotometric	29
30				30
25	benzene		calorimetry	17
30	chlorobenzene	$\Delta S = -79.5$ J K^{-1} mol^{-1}	spectrophotometric	13
–	benzene		calorimetry	16
25				17
	solid state		DSC	31
	benzene		calorimetry	17

TABLE 1 (continued)

L	X	Addend	$-\Delta H$ (kJ mol^{-1})	K
$PMePh_2$			57.3 ± 2.1	
PEt_2Ph			53.6 ± 1.7	
P(*p*-Tol)$_3$			48.5 ± 1.2	
$P(Bu^t)Ph_2$			25.1 ± 20.1	
PCy_3			no reaction	
PPh_3	Cl	CO	45.2	1250
P(*p*-Tol)$_3$	Cl	CF_3CH_2OH	12.1 ± 0.8	

TABLE 2

Thermochemical data for the reaction *trans*-[IrXL′L$_2$] with X–Y

L	X	L′	Addend	$-\Delta H$ (kJ mol^{-1})	K
PPh_3	Cl	CO	H_2	62.3	3.2×10^4
					1.5×10^4
				66.1	167
	Br			71.1	
				34.7	6100
	I			79.5	
				11.3	4760
P(*p*-Tol)$_3$	Cl			55.2	267
					4.4×10^4
P(*m*-Tol)$_3$					2.5×10^4
P(*p*-Anis)$_3$					5.2×10^4
PCy_3					2.4×10^3
				50.2	6.0×10^3
				44.8	95.2
	Br			51.9	1.14×10^3
	I			75.3	312
$P(OPh)_3$	Cl			51.5	580
	Br			40.6	2.1×10^3
	I			11.3	8.3×10^3
$P(Pr^i)_3$	Cl			44.4	610
	Br			54.8	1.6×10^3
	I			17.2	1.7×10^4
PEt_3	Cl			55.6	
$P(Bu^t)Ph_2$				48.1	847
$P(CH_2Ph)_3$				62.3	75.7
PPh_3	Cl	CO	Cl_2	339 ± 42	
			Br_2	247 ± 21	
				218 ± 2	

T (°C)	Solvent	Other	Method	Ref.
30–60			GLC	16
25			calorimetry	17
		$\Delta S = -92.0\ \mathrm{J\ K^{-1}\ mol^{-1}}$		13
30–60			GLC	16

T (°C)	Solvent	Other	Method	Ref.
30	chlorobenzene	$\Delta S = -121\ \mathrm{J\ K^{-1}\ mol^{-1}}$	spectrophotometric	13
	benzene			38
80	toluene		spectrophotometric	37
30	chlorobenzene	$\Delta S = -129.7\ \mathrm{J\ K^{-1}\ mol^{-1}}$	kinetic	36
80			spectrophotometric	37
30	chlorobenzene	$\Delta S = -113.0\ \mathrm{J\ K^{-1}\ mol^{-1}}$	spectrophotometric	13
80	toluene			
80				37
30	chlorobenzene		kinetic	30
				36
40				30
30				36
80	toluene			37,38
	chlorobenzene			36
80	toluene			37,38
25	benzene		calorimetry	17
				16

TABLE 2 (continued)

L	X	L′	Addend	$-\Delta H$ (kJ mol^{-1})	K
			I_2	136.4 ± 2.5	
				150.2 ± 0.8	
				143.9 ± 4.6	
				123.4 ± 9.2	
	F			146.9 ± 6.7	
	Br			148.5 ± 2.1	
	I			120.1 ± 5.0	
	NCS			138.5 ± 1.3	
	N_3			154.4 ± 3.8	
	C_6F_5			43.5 ± 4.2	
PMe_3	Cl			185.4 ± 7.1	
PMe_2Ph				173.6 ± 2.9	
$P(OPh)_3$				136.8 ± 0.8	
PEt_3				167.4 ± 1.0	
$PMePh_2$				160.2 ± 0.4	
PEt_2Ph				170.3 ± 6.0	
$P(Bu^t)Ph_2$				111.7 ± 1.7	
PCy_3				116.3 ± 3.3	
$AsPh_3$				171.5 ± 10.9	
$P(CH_2Ph)_3$				145.6 ± 1.4	
PPh_3	Cl		CS	145.6 ± 1.3	
	F	CO	o-$O_2C_6Cl_4$	139.3 ± 2.5	
	Cl			120.9 ± 1.7	
	Br			138.5 ± 3.8	
	I			123.0 ± 2.9	
	NCS			115.9 ± 2.1	
	N_3			135.1 ± 4.2	
PMe_3	Cl			154.0 ± 5.9	
PMe_2Ph				172.4 ± 2.1	
$P(OPh)_3$				127.6 ± 4.2	
PEt_3				190.0 ± 4.0	
$PMePh_2$				133.5 ± 0.8	
PEt_2Ph				165.3 ± 5.0	
$P(Bu^t)Ph_2$				123.0 ± 2.9	
$AsPh_3$				134.3 ± 0.8	
PPh_3	Cl	CS		143.1 ± 3.3	
		CO	HCl	88 ± 4	
			HBr	109 ± 8	
			HCl	98.8 (*cis*-chloro isomer) 9.7 (*trans*-chloro isomer)	
PMe_3	Cl	CO	HI	160.2 ± 2.9	
				167.8 ± 2.9	

T (°C)	Solvent	Other	Method	Ref.
				17
				16
	1,2-dichloroethane			17
	acetonitrile			
	benzene			
	1,2-dichloroethane			18
	benzene			17
	1,2-dichloroethane			19
				20
	benzene			17
	1,2-dichloroethane			18
				19
	benzene			17
220–234			DSC	47
240–258				
25	1,2-dichloroethane		calorimetry	18
	benzene			

TABLE 2 (continued)

L	X	L′	Addend	$-\Delta H$ (kJ mol^{-1})	K
			CH_3I	117.2 ± 6.7	
				117.6 ± 7.9	
			C_2H_5I	109.6 ± 2.9	
				107.1 ± 5.0	
			n-C_3H_7I	102.9 ± 3.8	
				102.1 ± 5.9	
PMe_3	Cl	CO	i-C_3H_7I	88.3 ± 9.6	
			$C_6H_5CH_2I$	94.9 ± 6.7	
			$CH_3C(O)I$	125.5 ± 4.2	
			$CH_3C(O)Cl$	122.2 ± 3.4	
				121.3 ± 4.2	
				152.0 ± 17.0	
PMe_2Ph				124.3 ± 5.4	
$P(OPh)_3$				70.7 ± 2.5	
PEt_3				120.5 ± 6.7	
			$CH_3C(O)Cl$	118.4 ± 6.7	
				156.1 ± 8.4	
$PMePh_2$				113.4 ± 4.6	
P(*p*-Tol)Ph_2				105.0 ± 2.9	
$P(Bu^t)Ph_2$				90.8 ± 1.7	
$P(CH_2Ph)_3$				75.3 ± 4.2	
PMe_2Ph	Cl	CO	C_2H_5-C(O)Cl	122.6 ± 4.6	
			i-C_3H_7-C(O)Cl	119.7 ± 4.2	
			$ClCH_2$-C(O)Cl	133.9 ± 3.4	
PMe_2Ph	Cl	CO	$ClCH_2$-C(O)Cl	139.8 ± 3.8	

T (°C)	Solvent	Other	Method	Ref.
	1,2-dichloroethane			
	standard state			
	1,2-dichloroethane			
	standard state			
	1,2-dichloroethane			
	standard state			
	1,2-dichloroethane			18
				48
	standard state			
	gas phase			
	1,2-dichloroethane			
	standard state			
	gas phase			
	1,2-dichloroethane			

TABLE 3

Thermochemical data for reactions of *trans*-[$RhXL'L_2$]

L	X	L'	Addend	$-\Delta H$ (kJ mol^{-1})	K
PPh_3	I	CO	$H_2C{=}CH_2$		<1
	Cl		$(NC)_2C{=}C(CN)_2$		508 ± 59
					370 ± 43
					330 ± 40
					58 ± 5
					2000 ± 700
					196 ± 16
P(*p*-Anis)$_3$					$1.3 \times 10^4 \pm 1.4 \times 10^3$
P(*p*-Tol)$_3$					$3.28 \times 10^3 \pm 4 \times 10^2$
P(*p*Cl-Tol)$_3$					69 ± 10
$P(OPh)_3$					115 ± 12
P(O-*o*-Tol)$_3$					34 ± 4
PPh_3	Br				56 ± 5
	NCS				99 ± 7
	NCO				560 ± 90
	Cl	CS			480 ± 62
	I	CO	C_2H_2		<1
	Cl		SO_2	33.05	
				28.9 ± 0.8	
PPh_3	Cl	CO	I_2	121.3 ± 0.8	
	Br			112.5 ± 4.2	
	I			95.8 ± 5.9	
$P(OMe)_3$	Cl	CO		108.4 ± 0.8	
PMe_3				146.0 ± 2.1	
PMe_2Ph				148.5 ± 0.8	
$P(OPh)_3$				88.7 ± 1.2	
$PMePh_2$				121.3 ± 1.7	
PEt_2Ph				143.9 ± 2.1	
PPh_3				121.3 ± 0.8	
$P(Bu^t)Ph_2$				174.9 ± 6.3	
PCy_3				84.1 ± 2.5	
$AsPh_3$				123.8 ± 1.2	
PPh_3	Cl	CS		114.2 ± 2.1	
		CO	*o*-$O_2C_6Cl_4$	102.5 ± 0.8	
	Br			105.0 ± 2.5	
	I			105.0 ± 4.6	
	Cl	CS		102.1 ± 4.6	
PMe_2Ph				123.4 ± 3.3	
$P(OPh)_3$				127.6 ± 0.4	
$PMePh_2$				97.9 ± 2.9	
PEt_2Ph				108.4 ± 2.1	
$P(Bu^t)Ph_2$				87.9 ± 2.4	
PCy_3				no reaction	
$AsPh_3$				97.5 ± 5.0	

T (°C)	Solvent	Other	Method	Ref.
20	chlorobenzene		spectrophotometric	24
15.5	acetone			11
25.0				
	tetrahydrofuran			
	benzonitrile			
34.5	acetone			
25.0				
20	chlorobenzene			24
154	solid		DSC	34
25	benzene		calorimetry	17

TABLE 4

Thermochemical data for oxidative addition reactions of cationic complexes

M	LL	Addend	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (J K^{-1} mol^{-1})
Co	*cis*-$Ph_2PCHCHPPh_2$	*o*-$O_2C_6Cl_4$	196.2 ±10.9	
Rh			144.1 ±13.9	
		O_2	46	
Ir		*o*-$O_2C_6Cl_4$	178.2 ±16.3	
	$Ph_2PCH_2CH_2PPh_2$	$(EtO)_3SiH$	75.52 ± 1.46	215.9 ± 5.0
			82.42 ± 1.88	232.2 ± 6.3
		$Me(EtO)_2SiH$	66.94 ± 1.46	195.4 ± 4.2
			71.54 ± 0.84	199.6 ± 2.9
		$Me_2(EtO)SiH$	57.02 ± 1.63	202.1 ± 6.3

$PPh_3 > AsPh_3 > P(Bu^t)Ph_2 \gg PCy_3$ (no reaction) [17]. The dependence of ΔH on anion for addition of olefins to *trans*-[$IrX(CO)(PPh_3)_2$] has been studied for C_2F_4 (solid state by DSC) [15] and $C_2(CN)_4$ [17]. In both cases $-\Delta H$ decreased in the order $Cl > F > Br > I$. In early work Vaska had found for ethylene addition that the reaction was slightly more exothermic for the iodo complex than for the chloro compound [13].

Relatively little work has been reported for addition of acetylenes. Vaska obtained ΔH and K for addition of acetylene to *trans*-[$IrCl(CO)(PPh_3)_2$] [13]. The anion dependence of $-\Delta H$ for $CF_3C{\equiv}CCF_3$ addition to *trans*-[$IrX(CO)(PPh_3)_2$] was $F > Cl > Br > I$ (solid state) [15]. For addition of $MeO_2CC{\equiv}CCO_2Me$ to a similar series of complexes $-\Delta H$ varied as $I > Br > Cl > F = N_3 > NCS$. The same order for Br and Cl held when the phosphine ligand was $PMePh_2$ [17].

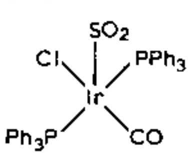
Less work has been done on rhodium complexes and only equilibrium constants for olefin additions are available. The dependence of K for TCNE addition on the phosphine ligand in *trans*-[$RhCl(CO)L_2$] varies as $P(p\text{-Anis})_3 > P(p\text{-Tol})_3 > PPh_3 > P(OPh)_3 > P(p\text{-Cl-Tol})_3 > P(O\text{-}o\text{-Tol})_3$. The anion dependence varied as $NCO > NCS > Br$ and the thiocarbonyl analog had a higher association constant than the carbonyl [11]. Vaska found that $K < 1$ for both C_2H_4 and C_2H_2 addition to *trans*-[$RhI(CO)(PPh_3)_2$] [23].

The study of dioxygen complexes of the platinum metals has been a subject of great interest but few thermochemical data are available [24–27]. The structure has been found to be that shown in I [28]. The trend in equilibrium constants for O_2 association with *trans*-[$IrX(CO)L_2$] is $I > Br > Cl > N_3 > NCO > F$ (for $L = PPh_3$) [29] and for $X = Cl$: $P(p\text{-Tol})_3 > PPh_3 > P(m\text{-Tol})_3 > PCy_3 > P(o\text{-Tol})_3$ [30]. A value of the enthalpy of association

K	T (°C)	Solvent	Method	Ref.
$>10^5$	25	1,2-dichloroethane	calorimetry	50
$>10^5$				
		chloroform	kinetic	51
$>10^5$		1,2-dichloroethane	calorimetry	50
117	25.1	tetrahydrofuran		52
206	25.6	acetonitrile		
35.4	25.0	tetrahydrofuran		
126	25.0	acetonitrile		
5.76	−10.3	acetonitrile		

has been derived from kinetic data for addition to *trans*-[IrCl(CO)$(PPh_3)_2$], $\Delta H = -71.5$ kJ mol^{-1} [13]. A differential scanning calorimetric study of the decomposition of [IrCl(CO)$(PPh_3)_2 \cdot O_2$] showed it to be exothermic by 92 ± 0.4 kJ mol^{-1} [31]. The relation of this value to the heat of addition of O_2 is not known.

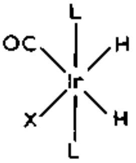
Addition of SO_2 to *trans*-[IrX(CO)L_2] has been studied. The structure of Ir(SO_2)(CO)Cl$(PPh_3)_2$ [32] and the analogous rhodium complex [33] has been found to be as shown below with a non-planar $IrSO_2$ unit. Independent determinations of the heat of addition of SO_2 for the case of $L = PPh_3$ and $X = Cl$ in benzene gave values which agreed within experimental uncertainties [16,17]. The value found from kinetic data in chlorobenzene [13] was slightly lower as was that determined in the solid state [31]. The dependence of $-\Delta H$ on anion was $F > Br > Cl > I$ [17]. The dependence on phosphine ligand was $PMe_2Ph > PMePh_2 > PEt_2Ph > P(p\text{-Tol})_3 > PPh_3 > P(Bu^t)Ph_2$ [PCy_3 and $P(OPh)_3$ no reaction] [17]. A value of -33.05 kJ mol^{-1} for the addition of SO_2 to *trans*-[RhCl(CO)$(PPh_3)_2$] in chlorobenzene was found [24]. A DSC study [34] gave a value of -28.9 ± 0.8 kJ mol^{-1}.



V

The value of ΔH for addition of carbon monoxide to Vaska's complex to give a five-coordinate complex has been found to be -45.2 kJ mol^{-1} [13]. A hydrogen-bonding interaction has been proposed to account for the observed $\Delta H = -12.1 \pm 0.8$ kJ mol^{-1} for the interaction of CF_3CH_2OH with *trans*-{IrCl(CO)[P(*p*-Tol)$_3$]$_2$} [17].

The structure of the dihydrogen adducts of square-planar iridium complexes is believed to be as shown below [2,35].

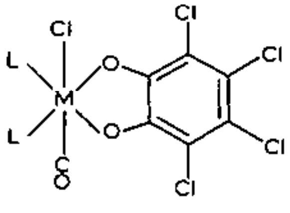


VI

Dihydrogen addition to iridium complexes, *trans*-[IrX(CO)L_2], has been studied by two groups. Vaska and co-workers have found that for $L = PPh_3$ $-\Delta H$ for H_2 addition increases in going from X = Cl to Br [13,36] but Strohmeier et al. [37,38] have found it to decrease in the order Cl > Br > I ($L = PPh_3$). For $L = P(OPh)_3$ the same order was found. When $L = PCy_3$ the same workers found the opposite order for halogen dependence and for $L = P(Pr^i)_3$ the order was Br > Cl > I. The dependence of ΔH and K on phosphine ligand (for X = Cl) is $PPh_3 > P(CH_2Ph)_3 > PEt_3 > P(OPh)_3 > PCy_3 > P(Bu^t)Ph_2 > P(Pr^i)_3 \approx PCy_3$. The position of PCy_3 is questionable since two different ΔH values have been reported [36,37]. Equilibrium constants give the order P(*p*-Anis)$_3$ > P(*p*-Tol)$_3$ > PPh_3 > P(*m*-Tol)$_3$ > PCy_3 [13,30,38].

Dihalogens are believed to add in a *trans* orientation to square-planar iridium and rhodium complexes [3,39], but there has been a suggestion of *cis*-addition [40]. The heats of dihalogen addition to rhodium and iridium complexes have been studied [17]. The reaction becomes less exothermic in the order $Cl_2 > Br_2 > I_2$. The values of ΔH for I_2 addition to *trans*-[IrCl(CO)$(PPh_3)_2$], in benzene, determined by Blake and co-workers [17] and by Drago et al. [16] differ by about 10%. The solvent dependence for I_2 addition shows the reaction to become less exothermic in the order 1,2-dichloroethane > benzene > acetonitrile. This is assigned primarily to the endothermic contribution required for destruction of the I_2–solvent interaction. The anion dependence for addition to *trans*-[MX(CO)L_2] follows the order (M = Ir and $L = PPh_3$) $N_3 > Br \approx F > NCS > Cl > I > C_6F_5$. For rhodium complexes the order is Cl > Br > I [17]. The phosphine dependence has been investigated in detail by Blake and co-workers [17]. The order of decreasing $-\Delta H$ for iridium is (in C_6H_6) $PMe_3 > PMe_2Ph > PEt_2Ph > PMePh_2 > PPh_3 \approx P(OPh)_3 > PCy_3 > P(Bu^t)Ph_2$. For rhodium the order is $PMe_3 \sim PMe_2Ph \sim PEt_2Ph > PMePh_2 \sim PPh_3 > P(OMe)_3 > P(OPh)_3 > PCy_3$. For complexes *trans*-[MCl(CS)$(PPh_3)_2$], $-\Delta H$ for I_2 addition was CS > CO for iridium and CO > CS for rhodium [17].

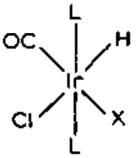
Addition of tetrachloro-*o*-benzoquinone to complexes has been studied. The geometry of the adduct has been established to be as shown for



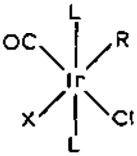
VII

L = PPh_3 and $PMePh_2$ [12,41,42]. For iridium complexes *trans*-[IrX(L′)L_2] the dependence of $-\Delta H$ on anion (L′ = CO and L = PPh_3) is NCS < Cl < I < N_3 ~ Br ~ I. For the corresponding rhodium complexes it was Cl ≈ Br ≈ I. In the case of iridium the thiocarbonyl complex underwent a more exothermic reaction than the carbonyl while in the case of rhodium CS ≈ CO. The dependence on phosphine ligand was for iridium ($-\Delta H$): PEt_3 > PMe_2Ph > PEt_2Ph > $AsPh_3$ ≈ $PMePh_2$ > $P(OPh)_3$ > $P(Bu^t)Ph_2$. The PCy_3 complex did not react. For rhodium the order ($-\Delta H$) was $P(OPh)_3$ > PMe_2Ph > PEt_2Ph > PPh_3 > $PMePh_2$ > $P(Bu^t)Ph_2$ [17].

Oxidative addition reactions in which a heteronuclear bond in the addend molecule is cleaved have been less well studied. Addition of hydrogen halides has been shown to occur via a *cis* addition [43–46] and organic halides have generally been found to give a *trans* addition as shown below [39,46–48].



VIII



IX

Hydrogen halide addition to *trans*-[IrCl(CO)L_2] has been studied. In benzene solution ΔH for HCl and HBr addition to the PPh_3 complex are -88 ± 4 and -109 ± 8 kJ mol^{-1} respectively [17]. A differential scanning calorimetric study of the decomposition of $IrCl_2H(CO)(PPh_3)_2$ has reported a value of $\Delta H = 98.8$ kJ mol^{-1} for HCl elimination from a compound identified as having structure VIII. A value of 9.7 kJ mol^{-1} was reported for the reaction of a "*trans*" isomer but this is apparently in error since the methods of preparation described give only isomer VIII [45]. $-\Delta H$ for addition of HI to the PMe_3 complex is 160.2 ± 2.9 kJ mol^{-1} in 1,2-dichloroethane and 167.8 ± 2.9 kJ mol^{-1} in benzene [18].

Addition of alkyl iodides to *trans*-$[IrCl(CO)(PMe_3)_2]$ has been studied [18]. The reaction becomes less exothermic in the order (1,2-dichloroethane) $CH_3 > C_2H_5 > n\text{-}C_3H_7 > CH_2C_6H_5 > i\text{-}C_3H_7$. The value of $\Delta H^{\ominus}$ was found to be the same as ΔH, within the limits of experimental uncertainty.

The ΔH for addition of acyl halides has been measured for a series of compounds [49]. For acetyl chloride addition the reaction becomes less exothermic in the order $PMe_3 \sim PMe_2Ph > PEt_3 > PMePh_2 > P(p\text{-Tol})Ph_2 > P(Bu^t)Ph_2 > P(CH_2Ph)_3 > P(OPh)_3$. The general trend as a function of substituent in the acyl chloride is $Cl_2CHC(O)Cl > ClCH_2C(O)Cl > CH_3C(O)Cl > C_2H_5C(O)Cl > i\text{-}C_3H_7C(O)Cl$. Sufficient data has been obtained to determine ΔH for the addition reaction of acetyl chloride to *trans*-$[IrCl(CO)(PMe_3)_2]$ in solution, standard state and gas phase.

Some of the previous studies of additions to rhodium and iridium complexes of the type *trans*-$[MCl(CO)L_2]$ have developed correlations of ΔH with steric and electronic properties of the tertiary phosphine ligands. Tolman's cone angle, θ, and electronic parameter, ν, provide values for a wide range of ligands [48]. Blake and co-workers have found a satisfactory fit of data using the following two-parameter relationship [17,49].

$$\Delta H = A_0 + A_1\theta + A_2\nu \tag{11}$$

Parameters for additions of I_2, SO_2, $(CN)_2C{=}C(CN)_2$, $o\text{-}O_2C_6Cl_4$ and $CH_3C(O)Cl$ are given in Table 4. An attempt was made to fit data from the literature [36,37] for H_2 additions to this type of relationship but a low correlation coefficient (0.2) was found.

A limited amount of work has been done on cationic complexes of the type $\{M[P{-}P]_2\}^+$ (M = Co, Rh or Ir and P—P = bidentate tertiary phosphine). These data are given in Table 5. The addition of tetrachloro-*o*-benzoquinone to complexes of *cis*-$Ph_2PCH{=}CHPPh_2$ showed the following metal dependence ($-\Delta H$) Co > Ir > Rh [50]. ΔH for addition of dioxygen to the rhodium complex has been determined [51]. Addition of silanes of the type $HSi(OEt)_n(Me)_{3-n}$ to $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$ has been studied. The reaction becomes more exothermic with an increasing number of ethoxy groups and for a given silane is more exothermic in acetonitrile than in tetrahydrofuran as solvent [52].

Calorimetric methods have been used to determine heats of reaction for a number of substances with ethylenebis(triphenylphosphine)platinum(0). These are summarized in Table 6. Heats of replacing ethylene by tetracyanoethylene [53], diphenylacetylene [54], carbon disulfide [55] and 3-phenylcyclobutene-1,2-dione [56] have been measured and are exothermic. The enthalpy of addition of diiodine, 1,2-diiodoethane and methyl iodide to the platinum(0) ethylene complex has been measured [57]. The heats of adding ethylene, styrene, *cis*- and *trans*-stilbene and carbon disulfide to bis(triphen-

TABLE 5

Fit of data for the reaction *trans*-[MCl(CO)L_2] + addend ⇌ 1 : 1 complex to a two-parameter equation of the type $-\Delta H$ (kJ mol^{-1}) = $A_0 + A_1\theta + A_2\nu$

Addend	M	A_0	A_1	A_2	R	Ref.
I_2	Ir	4164.3	−1.778	−1.824	0.96	17
	Rh	5410.8	−1.284	−2.477	0.85	
o-$C_6Cl_4O_2$	Ir	4318.7	−1.590	−1.912	0.91	
	Rh	−1032.2	−0.9540	0.6150	0.94	
$(CN)_2CC(CN)_2$	Ir	3181.1	−1.540	−1.389	0.97	
SO_2		−3778.6	−0.9832	1.920	0.94	
$CH_3C(O)Cl$		4881.2	−0.9325	−2.248	0.97	49
H_2 [a]		−1243.5	−0.001076	+0.6325	0.2	

[a] Calculated data from refs. 37 and 38.

ylphosphine)platinum(0) have been determined [58].

Heats of addition of one and two moles of hydrogen chloride gas to diphenylacetylenebis(triphenylphosphine)platinum(0) to give $Pt(PPh_3)_2Cl$-(*trans*-PhC=CHPh) and $Pt(PPh_3)_2Cl_2$ + *trans*-stilbene, respectively, have been reported [59]. Displacement of hydrogen chloride from *trans*-[$Pt(PPh_3)_2HCl$] by tetracyanoethylene was found to be exothermic [60]. Addition of tetracyanoethylene to *trans*-[$Pt(PMe_2Ph)_2(CH_3)Cl$] to give a 1 : 1 complex is an exothermic process.

The reactions of diphenylcyclopropenone and benzocyclobutene-1,2-dione with [$Pt(PPh_3)_2$(*trans*-PhCH=CHPh)] to give four- and five-membered metallocyclic compounds, respectively, have been studied by calorimetric methods [61]. Differential scanning calorimetry was used to measure the heat of removing sulfur dioxide from [$Pt(PPh_3)_3SO_2$] [62].

In some of the studies the data for heats of solution of reactants and products have been determined so that $\Delta H^{\ominus}$ could be calculated. Available data for solution in pure solvent are given in Table 7.

Limited data are available for heats of sublimation and vapor pressures of rhodium and iridium complexes, Table 8. Vrieze and co-workers have determined ΔH_{sub} for complexes of the type $M(acac)U_2$ (M = Rh or Ir, acac = acetylacetonate and U = CO or a monodentate olefin) [63]. Blake and co-workers have determined heats of sublimation of the pairs of iridium(I) and iridium(III) complexes of types [IrCl(CO)L_2] and {$IrCl_2[C(O)CH_3]$-(CO)L_2} where L = PMe_3 and PEt_3 [49]. Within the limits of experimental error the heats of sublimation of corresponding pairs of complexes were the same.

TABLE 6

Enthalpy data for reactions of platinum complexes

Reaction		Ref.
$Pt(PPh_3)_2(CH_2{=}CH_2)_{(s)} + C(CN)_2{=}C(CN)_{2(g)} \rightarrow Pt(PPh_3)_2[C(CN)_2{=}C(CN)_2]_{(s)} + CH_2{=}CH_{2(g)}$	$\Delta H_{25°C} = -155.8 \pm 8.0$ kJ mol^{-1}	53
$Pt(PPh_3)_2(CH_2{=}CH_2)_{(s)} + CPh{\equiv}CPh_{(s)} \rightarrow Pt(PPh_3)_2(CPh{\equiv}CPh)_{(s)} + CH_2{=}CH_{2(g)}$	$\Delta H_{25°C} = -82 \pm 12$ kJ mol^{-1}	54
$Pt(PPh_3)_2(CH_2{=}CH_2)_{(s)} + CS_{2(g)} \rightarrow Pt(PPh_3)_2(CS_2)_{(s)} + CH_2{=}CH_{2(g)}$	$\Delta H_{25°C} = -44.0 \pm 2.2$ kJ mol^{-1}	55
$(PPh_3)_2Pt_{(s)} + C_2H_{4(g)} \rightarrow (PPh_3)_2PtC_2H_{4(s)}$	$\Delta H_{25°C} = 11.6$ kJ mol^{-1}	58
$+ H_2C{=}CHC_6H_{5(g)} \rightarrow (PPh_3)_2Pt(H_2C{=}CHC_6H_5)_{(s)}$	$\Delta H_{25°C} = -29.7$ kJ mol^{-1}	
+ *cis*-$PhCH{=}CHPh_{(g)} \rightarrow (PPh_3)_2Pt(PhCH{=}CHPh)_{(s)}$	$\Delta H_{25°C} = -78.6$ kJ mol^{-1}	
+ *trans*-$PhCH{=}CHPh_{(g)} \rightarrow (PPh_3)_2Pt(PhCH{=}CHPh)_{(s)}$	$\Delta H_{25°C} = -96.9$ kJ mol^{-1}	
$Pt(PPh_3)_2(n\text{-}C_2H_4)_{(s)} + pcbd_{(g)} \rightarrow Pt(PPh_3)_2(n\text{-}pcbd)_{(s)} + C_2H_{4(g)}$		56
pcbd = 3-phenylcyclobutene-1,2-dione, $\mathrm{Ph}\overline{\mathrm{C{=}CHC(O)C}}\mathrm{O}$	$\Delta H_{r.t.} = -64.7 \pm 4$ kJ mol^{-1}	
$(PPh_3)_2Pt_{(s)} + CS_{2(l)} \rightarrow (PPh_3)_2PtCS_{2(s)}$	$\Delta H_{25°C} = -49.9 \pm 0.3$ kJ mol^{-1}	58
$(PPh_3)_3PtSO_{2(s)} \rightarrow (PPh_3)_3Pt_{(s)} + SO_{2(g)}$	$\Delta H_{25°C} = 60.7 \pm 4.2$ kJ mol^{-1} (DSC)	62
trans-$Pt(PMe_2Ph)_2MeCl_{(s)} + C(CN)_2{=}C(CN)_{2(g)} \rightarrow Pt(PMe_2Ph)_2MeCl[C(CN)_2{=}C(CN)_2]_{(s)}$	$\Delta H = -142 \pm 6$ kJ mol^{-1}	61
$Pt(PPh_3)_2(CH_2{=}CH_2)_{(s)} + I_{2(g)} \rightarrow$ *trans*-$Pt(PPh_3)_2I_{2(s)} + CH_2{=}CH_{2(g)}$	$\Delta H_{25°C} = -176.6 \pm 5.4$ kJ mol^{-1}	57

$\mathrm{Pt(PPh_3)_2(CH_2{=}CH_2)_{(s)} + CH_2ICH_2I_{(g)} \rightarrow \mathit{cis}\text{-}Pt(PPh_3)_2I_{2(s)} + 2(CH_2{=}CH_2)_{(g)}}$ $\Delta H_{25°C} = -107.8 \pm 6.0\ \mathrm{kJ\ mol^{-1}}$ 57

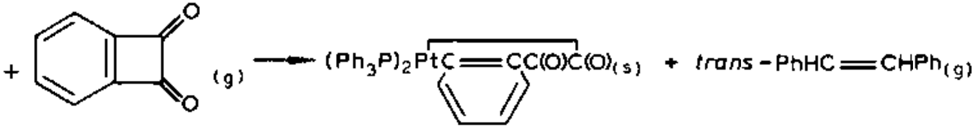
$\mathrm{Pt(PPh_3)_2(CH_2{=}CH_2)_{(s)} + CH_3I_{(g)} \rightarrow \mathit{cis}\text{-}Pt(PPh_3)_2(CH_3)I_{(s)} + CH_2{=}CH_{2(g)}}$ $\Delta H_{25°C} = -78.9 \pm 2.0\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{Pt(PPh_3)_2(CPh{\equiv}CPh)_{(s)} + HCl_{(g)} \rightarrow Pt(PPh_3)_2(Cl)(CPh{=}CPh)_{(s)}}$ $\Delta H_{25°C} = -90.2 \pm 6\ \mathrm{kJ\ mol^{-1}}$ 59

$\mathrm{Pt(PPh_3)_2(CPh{\equiv}CPh)_{(s)} + 2\ HCl_{(g)} \rightarrow \mathit{cis}\text{-}Pt(PPh_3)_2Cl_{2(s)} + \mathit{trans}\text{-}CHPh{=}CHPh_{(g)}}$ $\Delta H_{25°C} = -139.0 \pm 16\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{\mathit{trans}\text{-}Pt(PPh_3)_2HCl_{(s)} + C(CN)_2{=}C(CN)_{2(g)} \rightarrow Pt(PPh_3)_2[C(CN)_2{=}C(CN)_2]_{(s)} + HCl_{(g)}}$ $\Delta H = -112 \pm 6\ \mathrm{kJ\ mol^{-1}}$ 60

$\mathrm{Pt(PPh_3)_2(\mathit{trans}\text{-}PhHC{=}CHPh)_{(s)} + Ph\overline{C{=}CHC}(O)_{(g)} \rightarrow (Ph_3P)_2\overline{PtCPh{=}CPhC}(O)_{(s)} + \mathit{trans}\text{-}PhHC{=}CHPh_{(s)}}$ 61
$\Delta H = -94.8 \pm 6.0\ \mathrm{kJ\ mol^{-1}}$



$\Delta H = -57.1 \pm 5.1\ \mathrm{kJ\ mol^{-1}}$

TABLE 7

Heats of solution of some platinum and iridium complexes

Compound	Solvent	ΔH_{soln} (kJ mol^{-1})	Ref.
$IrCl(CO)(PPh_3)_2$	C_6H_6	2.17	31
$IrCl(CO)(PMe_3)_2$	1,2-$C_2H_4Cl_2$	17.1±4.1	18
$IrCl(CO)(PMe_3)_2 \cdot I_2$	1,2-$C_2H_4Cl_2$	18.1±1.0	
$IrCl(CO)(PMe_3)_2 \cdot CH_3I$	1,2-$C_2H_4Cl_2$	18.6±0.4	
$IrCl(CO)(PMe_3)_2 \cdot C_2H_5I$	1,2-$C_2H_4Cl_2$	15.9±0.8	
$IrCl(CO)(PMe_3)_2 \cdot (n\text{-}C_3H_7I)$	1,2-$C_2H_4Cl_2$	18.0±0.8	
$IrCl(CO)(PEt_3)_2 \cdot CH_3C(O)Cl$	1,2-$C_2H_4Cl_2$	17.5±0.7	41
trans-$Pt(PPh_3)_2I_2$	1,2-$C_2H_4Cl_2$	9.0±1.1	57
cis-$Pt(PPh_3)_2Cl(CPh{=}CHPh)$	1,2-$C_2H_4Cl_2$	15.9±0.8	59
$Pt(PPh_3)_2$(*cis*-PhHC=CHPh)	C_6H_6	13.1±1.8	58
$Pt(PPh_3)_2$(*trans*-PhHC=CHPh)	C_6H_6	10.9±0.2	
$Pt(PPh_3)_2(C_2H_4)$	C_6H_6	3.36	

TABLE 8

Heats of sublimation of rhodium and iridium complexes

Compound	ΔH_{sub} (kJ mol^{-1})	T (°K)	Vapor pressure (torr × 10^4)	Ref.
(acac)RhU_2				
U = CO	86.2± 2.9	300.9	28.5	63
C_2H_4	97.9± 3.8	300.9	5.3	
C_3H_6	86.2± 1.7	302.5	41.1	
C_2H_3Cl	117.2± 7.1	288.1	29.9×10^{-2}	
$C_2H_3O_2CCH_3$	121.3± 3.3	308.5	1.6×10^{-2}	
$CH_2{=}CHCO_2CH_3$	111.7± 4.6	310.7	3.0×10^{-2}	
(acac)IrU_2				
U = CO	92.0± 1.3	303.0	1.8	
C_2H_4	82.8± 4.1	302.2	2.1	
C_3H_6	90.0± 1.3	303.7	22.2	
C_2H_3Cl	89.5± 4.1	297.7	32.6×10^{-2}	
$C_2H_3O_2CCH_3$	120.5± 2.9	325.1	5.8×10^{-2}	
$CH_2{=}CHCO_2CH_3$	117.2± 5.0	325.0	5.2×10^{-2}	
$IrCl(CO)(PMe_3)_2$	67.4±15.5	372.1	198 ±17	48
$IrCl(CO)(PEt_3)_2$	79.5± 9.6	372.0	301 ± 4	
$IrCl_2(CO)[C(O)CH_3](PMe_3)_2$	67.4± 8.4	403.2	13.9± 0.5	
$IrCl_2(CO)[C(O)CH_3](PEt_3)_2$	71.6± 0.8	371.0	2.1± 0.3	

D. BOND ENERGIES

Mean bond dissociation energies have been approximated using eqn. (9) and the data for addition of dihalogens [16–18] or dihydrogen [36] to rhodium or iridium complexes. These values are given in Table 9. In $[IrCl(CO)(PPh_3)_2X_2]$ $\bar{D}$(Ir—X) decreases in the order $Cl > H > Br > I$. The value of $\bar{D}$(Ir—I) has a marked dependence on the phosphine ligand in $[IrCl(CO)L_2I_2]$ [17] and spans a range from 134 kJ mol^{-1} for the complex of PCy_3 to 190 ± 8 kJ mol^{-1} for that of PMe_3. The value for $\bar{D}$(Rh—I) is less than that of corresponding iridium complexes.

In complexes of the type $[IrClI_2(CO)(PMe_3)_2]$ Yoneda and Blake [18] adopted the method used by Mortimer et al. [57] to calculate a relative scale of values $D(Ir—R) - D_I(Ir—I)$ where the latter is the value of the first dissociation energy of $[IrClI_2(CO)(PMe_3)_2]$. In this series of complexes the relative order of Ir—R bond energy is $H > CH_3 \sim C_2H_5 \sim n\text{-}C_3H_7 > CH_3C(O) > i\text{-}C_3H_7 > C_6H_5CH_2$ [18]. An absolute value of the bond energy D(Ir—R) can be approximated by substituting $\bar{D}$(Ir—I) from $[IrClI_2(CO)(PMe_3)_2]$ for D_I(Ir—I). This gives $D(Ir—H) = 249 \pm 20$ kJ mol^{-1} which is comparable to that obtained by Vaska and Werneke for the dihydrogen adduct of *trans*-$[IrCl(CO)(PPh_3)_2]$ [36]. The difference $D(Ir—CH_3) - D_I(Ir—I) = 2 \pm 13$ kJ mol^{-1} is comparable to that found by Mortimer in *cis*-$[PtRI(PPh_3)_2]$, $D(Pt—CH_3) - D_I(Pt—I) = 6 \pm 5$ kJ mol^{-1} [57]. A value for the $Ir—C(O)CH_3$ bond energy in $\{IrCl_2[C(O)CH_3](CO)(PMe_3)_2\}$ of 205 ± 46 kJ mol^{-1} has been obtained from the heat of addition of acetyl chloride to *trans*-$[IrCl(CO)(PMe_3)_2]$ in the gas phase [49]. In earlier work a value of the incremental increase of $D(Ir—CF_nH_{3-n})$ of 15 kJ mol^{-1} per fluorine had been obtained from a DSC study of rates of the acyl to alkyl migration reaction in $\{IrCl_2[C(O)CF_nH_{3-n}](PPh_3)_2\}$ [64].

Calorimetric data for additions of hydrogen chloride to $[Pt(PPh_3)_2(PhC \equiv CPh)]$ have been used to calculate a value of 215 ± 23 kJ mol^{-1} for D[Pt—C(Ph)=CHPh] [59]. This is lower than the value obtained for $D(Pt—C_6H_5) = 264 \pm 15$ kJ mol^{-1} in *trans*-$[Pt(PEt_3)_2ClPh]$ [59,65]. $\bar{D}$[Pt—C(O)Ph] = 180 kJ mol^{-1} was found for *trans*-$\{Pt(PPh_3)_2(Cl)[C(O)Ph]\}$ [66]. For $Pt(n\text{-}C_5H_5)(CH_3)_3$, $\bar{D}(Pt—CH_3) = 160$ kJ mol^{-1} was determined from mass spectral experiments [67]. A differential scanning calorimetric study of the elimination of acetone from $Pt(CH_3)_2[C(O)CH_3]Cl(PMe_2Ph)_2$ gave a value of $\bar{D}(Pt—C) = 158$ kJ mol^{-1} [68]. Differential scanning calorimetry has been used to study elimination of propene from $PtX_2(CH_2CH_2CH_2)L_2$ where X = Cl or Br and L_2 is $(C_5H_5N)_2$, $(4\text{-}CH_3C_5H_4N)$, 2,2′-bipyridyl or ethylene diamine. Values of D(Pt—C) were in the range 112–124 kJ mol^{-1} and were in general slightly greater for bromo complexes than for the chloro compounds and increased in the order 4-methylpyridine < pyridine < bipyridine

TABLE 9

Approximated bond energies from oxidative addition and related studies

Parameter	Compound	Value (kJ mol^{-1})	Ref.
$\bar{D}$(Ir–Cl)	$[IrCl(CO)(PPh_3)_2Cl_2]$	297 ± 42	17
$\bar{D}$(Ir–Br)	$IrCl(CO)(PPh_3)_2Br_2$	222 ± 21	
		205	16
$\bar{D}$(Ir–I)	$[IrCl(CO)(PPh_3)_2I_2]$	146 ± 4	17
		151	16
	$[IrCl(CO)(PMe_3)_2I_2]$	190 ± 8	18
	$IrCl(CO)(PCy_3)_2I_2$	134 ± 5	
$\bar{D}$(Ir–H)	$[IrCl(CO)(PPh_3)_2H_2]$	251	36
$\bar{D}$(Rh–I)	$[RhCl(CO)(PPh_3)_2I_2]$	138 ± 3	17
$\bar{D}$(Ir–R) – $\bar{D}$(Ir–I)	$[IrCl(CO)(PMe_3)_2RI]$		
R = H		59 ± 12	18
CH_3		2 ± 13	
C_2H_5		−16 ± 12	
n-C_3H_7		−14 ± 13	
i-C_3H_7		−31 ± 16	
$CH_3C(O)$		−3 ± 16	
$C_6H_5CH_2$		−69 ± 16	
$\bar{D}$(Ir–C(O)CH_3)	$\{IrCl_2[C(O)CH_3](CO)(PMe_3)_2\}$	205 ± 46	49
$\bar{D}_1$(Pt–CH_3) – $\bar{D}_1$(Pt–I)	*cis*-$Pt(PPh_3)_2CH_3I$	+6 ± 5	57
$\bar{D}$(Pt–Ph)	$Pt(PEt_3)Ph_2$	264 ± 15	59, 65
$\bar{D}$(Pt–Cl)	$PtCl_2$	390 ± 3	
$\bar{D}$(Pt–CPh=CHPh)	$Pt(PPh_3)_2Cl(CPh{=}CHPh)$	215 ± 23	
$\bar{D}$(Pt–C(O)Ph)	$Pt(PPh_3)_2(Cl)[C(O)Ph]$	180	66
$\bar{D}$(Pt–CH_3)	$Pt(C_5H_5)(CH_3)_3$	160	67
$\bar{D}$(Pt–C)	$\{Pt(CH_3)_2[C(O)CH_3]Cl$-$[PMe_2Ph]_2\}$	158	68
2 $\bar{D}$(Pt–C) – $\bar{D}$(Pt–styrene)	$Pt(PPh_3)_2(C(Ph){=}C(Ph)CO)$	228 ± 26	63
2 $\bar{D}$(Pt–CH_3) – $\bar{D}$(Pt–styrene)	$Pt(PPh_3)_2(CH_3)_2$	209 ± 20	
$\bar{D}$(Pt–Cl) – $\bar{D}$(Pt–I)		82 ± 10	61
$\bar{D}$(Pt–tolane)	$Pt(PPh_3)_2(CPh{\equiv}CPh)$	389 ± 23	59
$\bar{D}$(Pt–Ph)	$Pt(PEt_3)_2(Cl)Ph$	264 ± 15	
$\bar{D}$(Pt–C)	$[PtCl_2(CH_2CH_2CH_2)]_4$	119.5	69
$\bar{D}$(Pt–C)	$PtCl_2py_2(CH_2CH_2CH_2)$	117.0	
$\bar{D}$(Pt–C)	$PtCl_2bipy(CH_2CH_2CH_2)$	121.4	

[69]. The relative values $\bar{D}$(Pt—C) − D(Pt—styrene) and 2$\bar{D}$(Pt—CH_3) − D(Pt—styrene) have been calculated to be 228 ± 26 and 209 ± 20 kJ mol^{-1} for $\{(Ph_3P)_2Pt[C(Ph){=}C(Ph)C(O)]\}$ and $Pt(PPh_3)_2(CH_3)_2$ respectively [63].

$\bar{D}$(Pt—Cl) has been estimated to be 390 ± 3 kJ mol^{-1} for $PtCl_2$ and this value has been used in subsequent derivations of bond enthalpies [59,65]. D(Pt—Cl) − D(Pt—I) has been calculated to be 82 ± 10 kJ mol^{-1} [61] which is much less than the difference found for iridium complexes, 150 ± 42 kJ mol^{-1} [16].

E. DISCUSSION

A sufficient number of reactions of comparable rhodium(I) and iridium(I) complexes have been studied to see that in general $\Delta H_{Rh} \approx 0.8\ \Delta H_{Ir}$, as can be seen in the plot of ΔH for rhodium vs. iridium complexes given in Fig. 2. This is in accord with the general view that adducts of rhodium(I) complexes are less stable than those of iridium(I) [70]. The position of cobalt in this trend is not well defined. Qualitative observations suggest the stability order Co > Ir > Rh [71]. This same order has been found for ΔH for addition of tetrachloro-1,2-benzoquinone to a series of cationic complexes [50]. The limited number of square-planar cobalt(I) complexes available for study along with rhodium and iridium analogs prevents better definition of the trend at present.

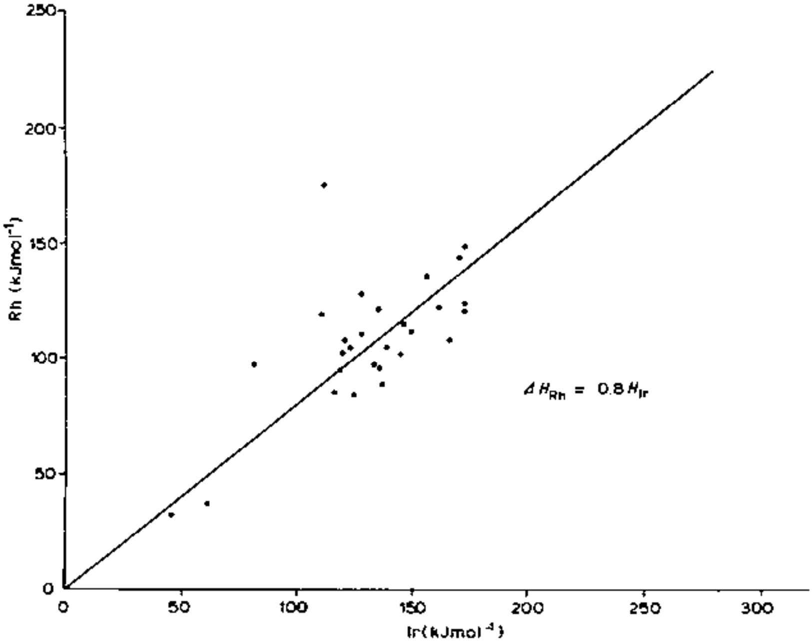


Fig. 2. Enthalpy changes for oxidative addition reactions of rhodium(I)(ΔH_{Rh}) versus iridium(I)(ΔH_{Ir}) complexes.

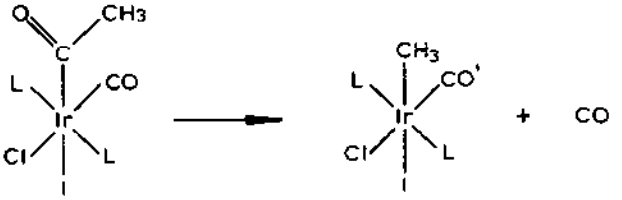
For complexes of the type *trans*-[$MX(CO)L_2$], studies have been carried out in which ΔH values have been obtained as a function of anion, X, and tertiary phosphine, L. No single trend is found for the anion dependence. This has been discussed in terms of a balance between increasing π-acceptor properties and decreasing electronegativity as one descends the halide group [15,17,72]. The case is more clear for the effect of tertiary phosphine ligand. The importance of the steric size of L on the stability of adducts has been recognized for some time. For example, dioxygen and dichlorine react rapidly with iridium(I) complexes of $PMe_2(Bu^t)$, more slowly with those of $PEt_2(Bu^t)$ but not at all with $PEt(Bu^t)_2$ complexes [73]. Shaw and co-workers studied this in a quantitative way in systems in which the relative equilibrium constant for protonation of iridium complexes was measured as a function of tertiary phosphine [73,74]. The trend observed in K for HCl addition was $PMe_2Ph > P(Bu^t)Me_2 > P(Bu^t)(Pr^n)_2 > P(Bu^s)_2Me > P(Bu^t)_2Et$. For addition of carboxylic acid the order was (with Tolman's [48] cone angle values, θ, and electronic parameter, ν, in parentheses) PMe_3 (118,2064.1) > PMe_2Ph (122,2065.3) > PEt_2Ph (136,2063.7) > $PMePh_2$ (136,2067.0) > PPh_3 (145,2068.0). It is not possible to clearly separate steric and electronic factors but steric size dominates in the pair $PMe_2Ph > PEt_2Ph$ while for equivalent cone angles the electronic factor is evident in $PEt_2Ph > PMePh_2$. The approach of Blake and co-workers [17,49] to fit ΔH values to a two-parameter equation linear in θ and ν has met with success in the cases studied (see Table 5). It remains to be seen whether failure of the model to fit existing data for dihydrogen additions is due to something unusual about the reaction or whether the data are not accurate.

The number of addition reactions of unsaturated molecules studied under comparable conditions is small. The general trend appears to be ΔH becoming more exothermic as the electronegativity of the substituents on the olefin increases. Tetracyanoethylene and hexafluorobut-2-yne produce the largest ΔH values. The dioxygen adducts of square-planar iridium(I) complexes have been a key model in structural studies [24] and in discussions of the activation of dioxygen by complexes [25–27]. Unfortunately, only the enthalpy for addition to Vaska's complex has been determined. More work is required on this important system.

For addition reactions which result in cleavage of the addend molecule and new bonds between the metal and both fragments, discussion of trends in ΔH is complicated. The value will depend on the dissociation energies of the bonds broken and the two new bonds to the metal. Studies of these systems have produced interesting data on bond dissociation energies for M—H, M—C and M—X bonds (see Table 9). These require the approximations discussed in eqns. (7) and (8) which have only been tested by actual determination of all of the parameters in the enthalpy cycle shown in Fig. 1

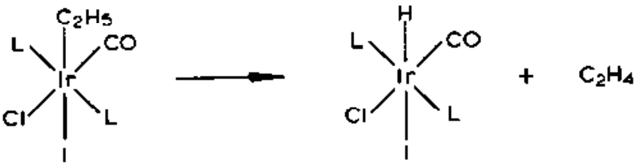
for one case. This was for the system *trans*-[IrCl(CO)L_2]/$CH_3C(O)Cl$ (L = PMe_3 or PEt_3) [49]. In this system the values of heats of sublimation of the square-planar reactant complex and of the six-coordinate product complexes were the same within experimental error as were the heats of solution. This supports the widely used approximation that that is the case. Data in Table 9 show that for iridium D(Ir—Z) falls in the order $Cl > H > Br > I \approx R$ (R = σ-bonded organic group) [16–18]. $D(Pt—CH_3)$ and $D(Ir—CH_3)$ are comparable in value [18,57,61] as are D(Pt—C(O)Ph) and $D(Ir—C(O)CH_3)$. For platinum, bonds to vinyl and aryl groups appear to be significantly stronger than those to the methyl group and bonds in the four-membered ring, $PtCH_2CH_2CH_2$, are weaker. Bond energies for organic compounds are available which can be combined with those for organometallic compounds to derive information on relevant heats of reaction.

Heats of formation are available for a wide range of organometallic compounds of the type $M(CO)_n(C_xH_y)$, which have only carbon monoxide and/or hydrocarbon ligands [76–78]. This is not the case for complexes containing tertiary phosphine ligands. Some of the studies referred to previously have obtained the data necessary to calculate $\Delta H^{\ominus}$ for the reaction studied by calorimetric methods [see eqns. (4) and (6)]. This makes it possible to calculate new $\Delta H^{\ominus}$ values for a number of interesting reactions since standard heats of formation are tabulated for organic and simple inorganic compounds [79,80]. This procedure has been illustrated by Yoneda and Blake [18] where $\Delta H^{\ominus}$ for carbon monoxide insertion, eqn. (12), and β-elimination, eqn. (13), were obtained (L = PMe_3). The work illustrates the potential value of data on heats of oxidative addition reactions in the calculation of data for heats of a variety of transformations important in organometallic chemistry and catalysis.



(12)

$\Delta H^{\ominus} = 46.8 \pm 14.2$ kJ mol^{-1}



(13)

$\Delta H^{\ominus} = 38 \pm 20$ kJ mol^{-1}

There is much work to be done in organometallic thermochemistry. For oxidative additions the H_2 and O_2 systems which are important models require additional data. More data on the steric and electronic effects of tertiary phosphine ligands are required to establish whether simple linear models can quantitatively account for steric and electronic effects. Studies of the addition of organic halides will yield important data on metal–carbon or hydrogen-bond energies and standard heats of reaction. This information may be of value in understanding why some reactions which seem plausible are rarely encountered, e.g. insertion of carbon monoxide into metal–hydrogen bonds.

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