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Enthalpy Changes in Oxidative Addition Reactions of Rhodium(I) and Iridium(I) Complexes

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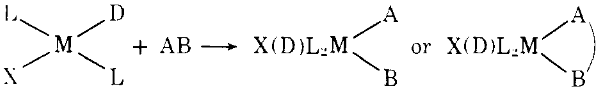
Abstract: Titration calorimetric methods have been used to determine enthalpies of oxidative addition reactions of iodine, tetrachloro-1,2-benzoquinone, tetracyanoethylene, sulfur dioxide, and dimethyl acetylenedicarboxylate with rhodium and iridium complexes of the type *trans*-[MX(CO)L_2] in benzene solution. X represents an anion and L represents triphenylarsine or a series of tertiary phosphorus ligands spanning a range of cone angles, θ, from 107 to 170° and a range of electronic parameters, ν (after C. A. Tolman), from 2056.4 to 2085.3 cm^{-1}. The data have been fitted to an empirical relation of the type $-\Delta H = A_0 + A_1\theta + A_2\nu$. Single parameter correlations were also attempted. Enthalpies for additions to *trans*-[MCl(CS)$PPh_3)_2$] were obtained for comparison with those of the carbonyl analogues. Enthalpies for addition of I_2, $C_2(CN)_4$, and *o*-$O_2C_6Cl_4$ to *trans*-[IrCl(CO)$(PPh_3)_2$] were also measured in the solvents 1,2-dichloroethane and acetonitrile (I_2 only). Enthalpies for the addition of HCl, HBr, Cl_2, Br_2, *o*-$(O_2N)C_6H_4SCl$, and *o*-$(O_2N)C_6H_4CH_2C(O)Cl$ to Vaska's complex and in some cases *trans*-[IrCl(CO)$(PMePh_2)_2$] were measured in benzene. The Cl_2, Br_2, and I_2 data were used to calculate approximations of the iridium–halogen bond energies. A new preparation for the complex *trans*-[IrCl(CO)$(PMe_2Ph)_2$] has been developed.

Introduction

We wish to report the results of our calorimetric study of oxidative addition reactions of rhodium and iridium complexes. Study of square-planar complexes with a d^8 electron configuration have provided much of the basis for current understanding of the factors influencing this important class of reactions. Interest has remained strong owing to the great synthetic utility of this reaction and its involvement in homogeneous catalytic reactions.[1-4] Complexes of the type *trans*-[MX(D)L_2] (M = Rh or Ir) have played a major role in studying substituent effects since complexes having a wide range of anion X, phosphorus ligand L, and π-acid ligand D can be prepared.[5] A major remaining goal is the quantitative characterization of the electronic and steric effects of the ligands, central metal, and added molecule, AB, on the kinetic and thermodynamic parameters for the reaction system shown in eq 1. To date much more work has been done concerning the kinetics of the reaction than the thermodynamic properties.



(1)

Kinetic data for reactions of O_2,[6,7] H_2,[6,7,8] HCl, and organic halides[9,10,11] has provided evidence for understanding trends in reaction rates primarily as a function of the electronic effect of ligands X and L as measured by the electronegativity of X,[6,11] summation of Hammett constants, $\Sigma\sigma^{\mathrm{ph}}$, for PR_3,[10] and electronic transitions in the M(I) complex.[6,9,12]

Quantitative correlations of rate with the steric effects of phosphorus ligands using Tolman's cone angle parameter θ[13] have not been developed since in general only ligands, L, with a narrow range of cone angles have been studied. Qualitative observations have demonstrated that steric factors do influence the rate markedly. For example, dioxygen and dichlorine react rapidly with iridium complexes of PMe_2(*t*-Bu), more slowly with PEt_2(*t*-Bu), and not at all with PEt(*t*-Bu)$_2$ complexes.[14] Steric effects have similarly been used to explain the failure of iridium complexes of P(*o*-Tol)$_3$ to react with H_2 and O_2 even though spectroscopic data for the complex are similar to those of reactive complexes.[15]

Equilibrium constants for a number of reactions of Vaska's complex, *trans*-[IrCl(CO)$(PPh_3)_2$], have been measured by spectroscopic methods. In the case of H_2,[4,16] O_2,[4] CO,[4] C_2H_4,[4] SO_2,[4] maleic anhydride,[17] and dimethyl maleate[17] the enthalpy changes have been evaluated from the temperature dependence of K. Differential scanning calorimetry has been used to measure ΔH for the elimination of SO_2,[18] O_2,[18] C_2F_4,[19] and $CF_3C{\equiv}CCF_3$[19] from Vaska's complex, and in the case of C_2F_4,[20] its fluoro, bromo, and iodo analogues. The dependence of ΔH on the nature of the phosphine ligand, L, has been determined for only a few compounds. Strohmeier has reported that $-\Delta H$ for reaction of olefins[17] with iridium complexes decreases in the order $P(OPh)_3 > PPh_3 > P(Cy)_3$ and for H_2,[16] $PPh_3 > P(OPh)_3$. Shaw and co-workers have determined the equilibrium constant for protonation of iridium complexes by benzoic acid or HCl in ethanol-benzene mixtures as a function of phosphorus ligand but ΔH values were not obtained.[14,21] Only in the case of SO_2 have thermodynamic values for analogous pairs of rhodium and iridium complexes been obtained ($-\Delta H$ Ir > Rh).[22] Other, indirect evidence has been used to suggest that heats of reaction should decrease in the order Ir > Rh.[22]

The enthalpy change for reaction 1 can provide important information about the electronic effects of X, D, and L and the steric effect of L on the reaction and on the activation of molecules by coordination to a metal atom. The activation of molecules by an oxidative addition process is in part a consequence of the alteration of bonds and their strengths upon coordination. For example, oxidative addition of H_2 replaces the strong H–H bond with two weaker M–H bonds.[23] This aspect of oxidative addition has recently been discussed from a theoretical point of view by Hoffman and co-workers.[24]

Methods previously used for determining ΔH have been of limited applicability. Equilibrium data are not reliable for $K > 10^3$ and are time consuming to obtain for a large number of reactions. The DSC method is only applicable to solid complexes which readily lose a volatile molecule. Tolman[13] has provided an extensive set of electronic and steric parameters, ν and θ, respectively, for phosphorus ligands but the development of reliable correlations of these parameters with enthalpy data requires that a much wider range of complexes be studied than has previously been the case. Successful correlation of the ΔH data by a relation of the type

$$-\Delta H = A_0 + A_1\theta + A_2\nu \qquad (2)$$

would be of very great predictive value. Tolman[13] has suggested that such an equation might apply to properties of ter-

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Table I. Enthalpy Data, $-\Delta H$ (kcal/mol),[a,b] for Oxidative Addition Reactions of Rhodium(I) and Iridium(I) Complexes, *trans*-[MX(CO)L_2] and *trans*-[MCl(CS)(PPh$_3$)$_2$], in Benzene

X	L	M = Ir				M = Rh		θ^c	ν^c
		I_2	*o*-$O_2C_6Cl_4$	$(NC)_2C_2(CN)_2$	SO_2	I_2	*o*-$O_2C_6Cl_4$		
F	PPh$_3$	35.1 ± 1.6	33.3 ± 0.6	23.9 ± 0.1	12.8 ± 0.5			92	
Cl		32.6 ± 0.6	28.9 ± 0.4	19.9 ± 0.2	11.4 ± 0.6	29.0 ± 0.2	24.5 ± 0.2	102	
Br		35.5 ± 0.5	33.1 ± 0.9	18.6 ± 0.6	11.5 ± 0.6	26.9 ± 1.0	25.1 ± 0.6	105	
I		28.7 ± 1.2	29.4 ± 0.7	12.6 ± 0.7	8.3 ± 0.9	22.9 ± 1.4	25.1 ± 1.1	107	
NCS		33.1 ± 0.3	27.7 ± 0.5						
N$_3$		36.1 ± 0.9	32.3 ± 1.0						
C$_6$F$_5$		10.4 ± 1.0	0[d]						
Cl	P(OMe)$_3$					25.9 ± 0.2	63.1 ± 1.4	107	2079.5
Cl	PMe$_3$					34.9 ± 0.5	61.2 ± 1.7	118	2064.1
	PMe$_2$Ph	41.5 ± 0.7	41.2 ± 0.5	28.3 ± 0.9	14.1 ± 2.6	35.5 ± 0.2	29.5 ± 0.8	122	2065.3
	P(OPh)$_3$	32.7 ± 0.2	30.5 ± 1.0	20.9 ± 1.0	~0[d]	21.2 ± 0.3	30.5 ± 0.1	128	2085.3
	PMePh$_2$	38.3 ± 0.1	31.9 ± 0.2	25.0 ± 0.2	13.7 ± 0.5	29.0 ± 0.4	23.4 ± 0.7	136	2067.0
	PEt$_2$Ph	40.7 ± 1.5	39.5 ± 1.2	26.5 ± 0.2	12.8 ± 0.4	34.4 ± 0.5	25.9 ± 0.5	136	2063.7
	PPh$_3$	32.6 ± 0.6	28.9 ± 0.4	19.9 ± 0.2	11.4 ± 0.6	29.0 ± 0.2	24.5 ± 0.2	145	2068.0
	P(*t*-Bu)Ph$_2$	26.7 ± 0.4	29.4 ± 0.7	16.3 ± 0.7	6.0 ± 4.8	41.8 ± 1.5	21.0 ± 0.6	157	2064.7
	P(Cy)$_3$	27.8 ± 0.8	~0[d]	~0[d]	~0[d]	20.1 ± 0.6	~0[d]	170	2056.4
	AsPh$_3$	41.0 ± 2.6	32.1 ± 0.2	19.7 ± 0.5		29.6 ± 0.3	23.3 ± 1.2		
			MCl(CS)(PPh$_3$)$_2$						
		34.8 ± 0.3	34.2 ± 0.8			27.3 ± 0.5	24.4 ± 1.1		

[a] 1 kcal = 4.184 kJ. [b] Error limits are one standard deviation. [c] From ref 13. [d] A value of 0 indicates that no reaction occurred.

tiary phosphine complexes including heats of reaction but no test has been published to date.

This report details our application of enthalpimetric titrations to the determination of enthalpy changes for oxidative addition reactions. This method has been applied to the study of reaction of unsaturated compounds with nickel(0)[25] and platinum(0)[26] compounds but not to the oxidative addition reaction of d^8 complexes. The method has made it possible to obtain enthalpy data for reactions of I_2, *o*-$O_2C_6Cl_4$, $C_2(CN)_4$, SO_2, and other small molecules with rhodium and iridium complexes of phosphorus ligands having a wide range of ν and θ values. The dependence of ΔH on the anion X and molecule D has also been studied. This has provided the data base necessary to fit ΔH values to eq 2.

Experimental Section

The following complexes [MX(CO)L_2] were prepared by methods in the literature (M = Ir, L = PPh$_3$ and X = F,[27] Cl,[28] I,[29] NCS,[29] N$_3$,[29] or C$_6$F$_5$;[30] X = Cl and L = P(OPh)$_3$,[31] AsPh$_3$,[31] PMePh$_2$,[32] PEt$_2$Ph,[33] P(*t*-Bu)Ph$_2$,[33] or PCy$_3$;[31] M = Rh, L = PPh$_3$ and X = Cl, Br or I;[34] X = Cl and L = AsPh$_3$).[34] The compounds where X = Cl and L = P(OMe)$_3$, PMe$_3$, PMe$_2$Ph, PMePh$_2$, PEt$_2$Ph, PPh$_3$, or P(OPh)$_3$ were prepared by addition of a slight excess of ligand to [RhCl(CO)$_2$]$_2$.[35] The complexes *trans*-[MCl(CS)PPh$_3$)] (M = Rh[36] or Ir[37]) were prepared by methods in the literature. Purity of the complexes was checked by IR and melting point. Benzene was distilled and stored over molecular sieves. Acetonitrile was distilled from P_4O_{10}. Iodine (Baker), dimethyl acetylenedicarboxylate (Eastman) (purity checked by ^{1}H NMR), and tetrachloro-1,2-benzoquinone (Aldrich) were the best available grade. Tetracyanoethylene (Eastman) was sublimed and sulfur dioxide (Matheson) was passed through a concentrated sulfuric acid trap before use. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer.

***trans*-[IrCl(CO)(PMe$_2$Ph)$_2$].** The following operations were carried out under a nitrogen atmosphere, except as noted. Dimethylphenylphosphine (0.38 mL) was added to a suspension of *trans*-[IrCl(CO)-(PPh$_3$)$_2$] (1.0 g) in 30 mL of ether. The mixture gradually became clear upon stirring for 2.5 h. Hexane (30 mL) was added and the volume of the mixture was reduced to about 30 mL by evaporation under a flow of N_2. The resulting yellow solid was recovered by filtration open to the atmosphere. The solid was recrystallized by dissolving in 30 mL of 9:1 ether-dichloromethane, filtering the solution, and adding 30 mL of hexane to the filtrate. Upon evaporation to about 30 mL, yellow crystals formed. The recovered yield was 0.3 g (45%), mp 120-123 °C (lit. 116-122 °C).[38]

Calorimetry. The Tronac 450-4 calorimeter system has been previously described.[39] For this project the reaction Dewar head was modified to accept a Teflon line for purging the vessel with argon. Solid samples of the metal complex (5-20 mg) were placed in the Dewar and the vessel was purged with argon for 20-30 min. Solvent (30-40 mL) was then added via syringe through the gas delivery line. In those cases where the equilibrium constant for reaction was $>10^3$ (I_2, TCNE, *o*-$O_2C_6Cl_4$, and SO_2) an excess of titrant solution, 0.1-0.3 M, was added via the micrometer syringe. Saturated solutions of SO_2 in benzene were used (~0.5-1.0 M). Enthalpy changes were calculated directly from the titration curve[40] and heats of dilution were found to be negligible. The reactions usually reached completion when the ratio of moles titrant:moles metal was about 1.1 to 1.3.

The calibration of the standard resistance heater was periodically checked by measuring the heat of reaction of 0.100 M aqueous HCl with tris(hydroxymethyl)aminomethane (THAM). Observed values were, for example, −11.48, −11.30 ± 0.24, and −11.48 kcal/mol (lit.[40] −11.35 kcal/mol).

Equilibrium constants (when $K < 10^4$) and enthalpies for reactions of dimethyl acetylenedicarboxylate were determined using the method of Drago[41] for fitting the best K and ΔH to heat changes for incremental additions of titrant solution. This data is available in the microfilm edition.

Enthalpy change values in Tables I-III are the averages of four to eight determinations using at least two independently prepared samples of the metal complex. Error limits are the standard deviation for the experimental values.

Table II. Thermodynamic Parameters for the Addition of Dimethyl Acetylenedicarboxylate to *trans*-[IrX(CO)L_2] in Benzene Solution

X	L	$K \times 10^{-2}$, M^{-1}	$-\Delta H$, kcal/mol[a,b]
F	PPh$_3$	13.2	12.6 ± 0.1
Cl	PPh$_3$	8.4	14.6 ± 0.1
Br	PPh$_3$	~2 × 10^4	14.9 ± 0.3
I	PPh$_3$	$>10^5$	15.4 ± 0.3
NCS	PPh$_3$	0.76	8.0 ± 0.6
N$_3$	PPh$_3$	35.3	12.6 ± 0.3
Cl	PMePh$_2$	$>10^4$	15.0 ± 0.3
Br	PMePh$_2$	$>10^4$	15.7 ± 0.2
Cl	AsPh$_3$	$>10^4$	13.2 ± 0.1

[a] 1 kcal = 4.184 kJ. [b] Error limits are one standard deviation.

Results

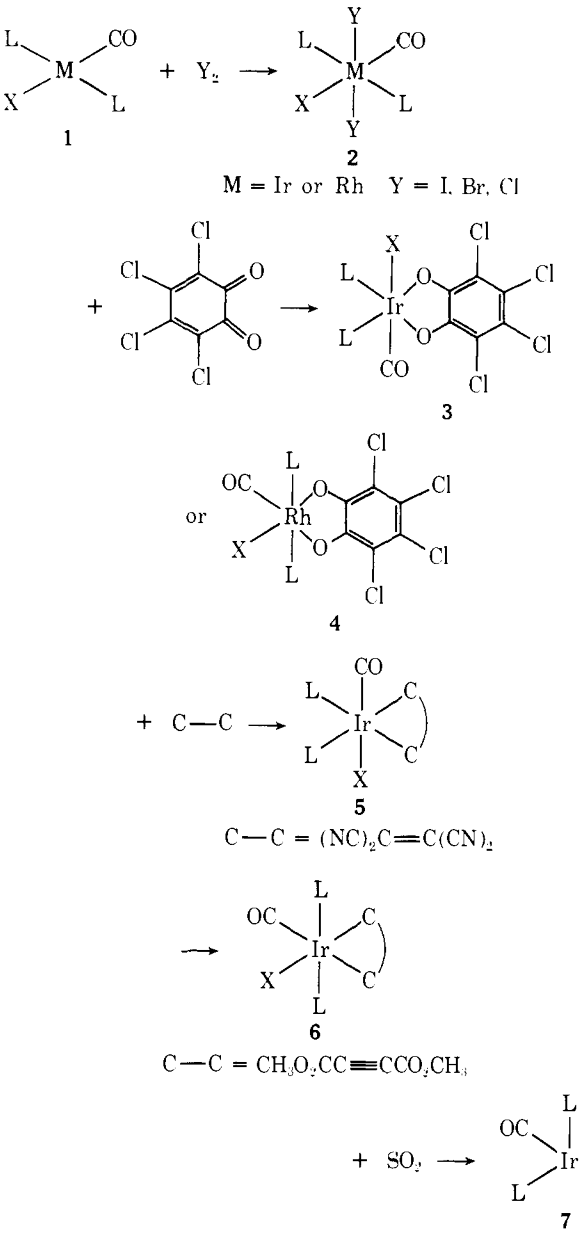
We have used the technique of thermometric titrimetry[40] to determine enthalpy changes for the following reaction system in benzene solution (Scheme I) (L = tertiary phosphine and X = anion).

Table III. Enthalpy Changes and Approximated Ir–X Dissociation Energies ($-\Delta H$, kcal/mol)[a,b] for Addition of Halogen-Containing Compounds to *trans*-[IrCl(CO)L_2] in Benzene

X–Y	L: PPh_3	L: $PMePh_2$	calcd D_A(Ir–X)[c]
HCl	21.0 ± 1.0	26.0 ± 1.2	
HBr	26 ± 2		
Cl_2	81 ± 10		71 ± 10
Br_2	59 ± 5		53 ± 5
o-$(O_2N)C_6H_4SCl$	29 ± 2	36.0 ± 1.0	
o-$(O_2N)C_6H_4CH_2C(O)Cl$		100 ± 25	
H_2	15		60[d]
I_2	32.6 ± 0.6	38.3 ± 0.1	35 ± 1

[a] 1 kcal = 4.184 kJ. [b] Error limits are one standard deviation. [c] L = PPh_3. [d] See ref 23.

Scheme I



Thermodynamic data are given in Tables I and II. Many examples of complexes of the type formed in these oxidative addition reactions have been prepared and characterized previously. The addition of halogens to square-planar rhodium and iridium[4,32,42,43] complexes, **1**, has been found to give the trans isomer shown, **2**. Addition of tetrachloro-*o*-quinone has been shown to give the isomer with cis phosphine ligands when M = Ir and L = PPh_3 or $PMePh_2$, **3**, and the isomer with trans phosphine ligands when M = Rh and L = PPh_3 or $PMePh_2$, **4**.[44,45] Tetracyanoethylene[46] also adds to square-planar iridium(I) complexes to give the adduct having *cis*-PPh_3 ligands, **5**. The geometry of the dimethyl acetylenedicarboxyate complex is not well characterized but the complex with L = $PMePh_2$ was found to have the phosphine ligands trans, **6**.[29] The structure of the SO_2 adduct of Vaska's complex has been determined.[47] Not all of the combinations of metal complexes and added molecule we have studied in this work have been characterized in detail. The geometries for compounds in each series are assumed for the present to be the same as the known, characterized examples. We have also measured ΔH for some reactions of the thiocarbonyl complexes, *trans*-[MCl(CS)$(PPh_3)_2$] (M = Rh or Ir). Some oxidative addition reactions of these compounds have been previously reported.[36,37,48]

Table III contains calorimetric data for the addition of HCl,[49] HBr,[49] Cl_2, Br_2,[32,43] *o*-$(O_2N)C_6H_4SCl$,[50] and *o*-$(O_2N)C_6H_4CH_2C(O)Cl$[51] to Vaska's complex or the methyldiphenylphosphine analogue. Previous synthetic work on these reactions is described in the references given. These substances, owing to their corrosive nature and reactivity toward water, presented a number of experimental difficulties in our calorimeter system. They were added to the metal complexes as benzene solutions and the enthalpy values in the table have been corrected for heats obtained by addition of solutions of the reagents to pure solvent. While the error limits are large in some cases, the data are indicative of the magnitudes of the heat changes to be expected for these substances.

The stoichiometry of the addition of substances of interest here to compounds of the type *trans*-[MX(CO)L_2] has been indicated by past synthetic work to be 1:1. This is also established by the thermometric titration curves obtained in this study. In the cases of some compounds (HCl, I_2, *o*-$O_2C_6Cl_4$) preformed samples of their adducts with *trans*-[IrCl(CO)$(PPh_3)_2$] were titrated with solutions of the compound and found to give no heat change, indicating that the product, once formed, does not react further.

In the case of SO_2 a number of 1:1 complexes have been characterized but 2:1 interactions have been observed.[47] No information is available concerning the relative magnitude of equilibrium constant for formation of 1:1 and 2:1 (SO_2:metal) complexes. In order to drive the reaction to completion an excess of SO_2 had to be used so the titration curves yield no data about stoichiometry. Since most complexes formed between SO_2 and the type of iridium(I) compounds used in this study are 1:1, we have assumed this stoichiometry. Our value of $\Delta H = -11.4 \pm 0.6$ kcal/mol for addition of SO_2 to *trans*-[IrCl(CO)$(PPh_3)_2$] compares favorably with that obtained by Vaska in chlorobenzene (10.1 kcal/mol, $K = 1.5 \times 10^3$ M^{-1})[4] but is higher than that obtained by DSC methods (9.6 ± 0.2 kcal/mol).[18]

Since dioxygen complexes are a potential impurity in samples of many of the iridium(I) complexes and might give rise to spurious heat effects, we titrated preformed [IrCl(CO)$(PPh_3)_2 \cdot O_2$] with I_2, *o*-$O_2C_6Cl_4$, and TCNE in benzene. In all cases there was no heat change.

With the exception of some of the dimethyl acetylenedicarboxylate complexes, the equilibrium constants for the reactions were $>10^3$ so that the enthalpy changes could be calculated directly from the titration curves. For the reactions of dimethyl acetylenedicarboxylate, both ΔH and K were obtained from titration data using the method of Drago[41] in those cases where $K < 10^3$. In a few reactions no heat change was observed. In those cases (Table I) a value of 0 means that no heat was evolved when the reactants were mixed, which occurred in five reactions. This could mean that $\Delta H = 0$ but is more likely the result of there being no reaction during the time scale of the experiment owing to the reaction being kinetically slow.

In order to assess the magnitude of solvent effects on ΔH values we have obtained data for the reaction of Vaska's complex with I_2, TCNE, and o-$O_2C_6Cl_4$ in the solvent 1,2-dichloroethane and with I_2 in acetonitrile. These data are given in Table IV.

Discussion

Solvent Effects. Enthalpy changes for reaction 1 measured in solution, ΔH_{meas}, will include the following contributions:

$$\Delta H_{\text{meas}} = \Delta H_{\text{react}} - \Delta H_{\text{solv,M(I)}} + \Delta H_{\text{solv,M(III)}} - \Delta H_{\text{solv,AB}} \quad (3)$$

where ΔH_{react} would be the heat of reaction in the absence of solvent effects, $\Delta H_{\text{solv,M(I)}}$ is the enthalpy of $MX(CO)L_2$–solvent interaction, $\Delta H_{\text{solv,M(III)}}$ is the heat of $MX(CO)L_2 \cdot AB$–solvent interaction, and $\Delta H_{\text{solv,AB}}$ is the enthalpy of the solvent interaction with the added molecule.

Benzene, used as the reaction solvent, can function to some extent as a Lewis base toward the acceptor molecules I_2, TCNE, o-$O_2C_6Cl_4$, and SO_2.[52] This interaction will be a constant contribution to the observed enthalpy changes for reactions of these molecules with the metal complexes. The magnitude of this interaction in the case of I_2 is -1.4 ± 0.8 kcal/mol.[53] Since this is due to the specific I_2–C_6H_6 interaction, data in Table I can be corrected by adding this amount to each ΔH value as has been suggested by Drago.[54] The E and C method of Drago provides a value of -2.7 kcal/mol for the SO_2–C_6H_6 interaction[54] and the experimentally obtained value for TCNE–C_6H_6 is -3.6 ± 0.1 kcal/mol.[55]

The solvent 1,2-$C_2H_4Cl_2$ should interact only weakly with the added nonpolar molecules and complexes used in this study.[56,57] We are assuming that $\Delta H_{\text{solv,AB}}$ is zero in 1,2-$C_2H_4Cl_2$. The difference $\Delta H_{\text{meas},C_6H_6} - \Delta H_{\text{meas},C_2H_4Cl_2}$ will then give a measure of the magnitude of the total of the three solvation terms in eq 3. This quantity is 1.8 ± 1.7 for I_2, 5.5 ± 0.8 for TCNE, and 4.2 ± 0.6 for o-$O_2C_6Cl_4$. For I_2 the difference can be accounted for by the I_2–C_6H_6 interaction indicating that the combination of the heat of solvation terms of the M(I) and M(III) complexes is about zero. This may indicate that the heats of solvation of M(I) and M(III) are similar in magnitude and cancel each other. For TCNE there is a significant residual, 1.9 ± 0.9 kcal/mol, after correction for the TCNE–C_6H_6 interaction due to the solvation of M(I) and M(III) in the two solvents. This is not unexpected since there is a change in the relative phosphine geometry in this reaction from *trans*-ML_2 to *cis*-ML_2 and the solvation terms might not cancel. A similar effect may be present in the o-$O_2C_6Cl_4$ reaction. The enthalpy of the interaction of this quinone with C_6H_6 is not known but may be similar to that for interaction of p-$O_2C_6F_4$ with benzene, where the value is -2.0 kcal/mol.[58] This would make the combined solvation terms for the M(I) and M(III) complexes about 2 kcal/mol.

The enthalpy of reaction of I_2 with Vaska's complex in acetonitrile is 4.9 ± 3.3 kcal/mol less exothermic than that in 1,2-dichloroethane. The enthalpy for the I_2–CH_3CN interaction is -1.9 ± 0.6 kcal/mol,[59] indicating that the combined solvation terms for the metal complexes again are not zero.

Metal Effects. Comparison of rhodium and iridium complexes using the data in Table I reveals that on the average the ΔH for reactions of rhodium complexes are about two-thirds the magnitude of those for the iridium analogues. This is likely to be a general trend and a factor in the increased lability and decreased stability of rhodium complexes formed by oxidative addition in comparison with iridium analogues.[22] Qualitatively this is illustrated by the ready isolation of complexes of the type $MCl(CO)L_2 \cdot O_2$ for iridium but not rhodium.[60]

Table IV. Solvent Dependence of $-\Delta H$ (kcal/mol)[a,b] for Oxidative Addition Reactions of *trans*-[IrCl(CO)(PPh$_3$)]

solvent	I_2	$C_2(CN)_4$	o-$O_2C_6Cl_4$
C_6H_6	32.6 ± 0.6	19.9 ± 0.2	28.9 ± 0.2
1,2-$C_2H_4Cl_2$	34.4 ± 1.1	25.4 ± 0.6	33.1 ± 0.2
CH_3CN	29.5 ± 2.2		

[a] 1 kcal = 4.184 kJ. [b] Error limits are one standard deviation.

Anion Dependence. The dependence of enthalpy changes on the anion in the iridium complexes is variable. For the reaction of $(MeO_2C)_2C_2$ the ΔH becomes more exothermic with decreasing electronegativity (F < Cl < Br < I). For TCNE and SO_2 the orders are reversed: I < Br < Cl < F. ΔH for reaction with I_2 and o-$O_2C_6Cl_4$ does not vary directly with the electronegativity of X but becomes more exothermic in the order I < Br > Cl < F. Mortimer and co-workers have found that the enthalpy for addition of C_2F_4 or C_4F_6 to *trans*-[IrX(CO)(PPh$_3$)$_2$] (obtained by DSC methods)[19] also goes through a minimum, I > Br < Cl < F. This variability of the halogen effect may reflect, as discussed by Mortimer and co-workers[19] and Vaska et al.,[12,61] a balance between the electron donor properties of the halogens and their π-acceptor capability. These two groups have discussed the effect of the anion in terms of its σ-donor and π-acceptor properties, the former contributing to metal electron density and the latter removing metal π-electron density. They would each reach a maximum at iodine and a minimum at fluorine. The strong π-acceptor groups (TCNE, SO_2) are most influenced by the competition for metal π density and enthalpies for the weaker π acceptor, $MeO_2CC{\equiv}CCO_2Me$, are most sensitive to the electronegativity of the anion X. I_2, o-$O_2C_6Cl_4$, C_2F_4, and C_4F_6 show intermediate behavior. Superimposed on the possible electronic effects of the halide ions is the steric effect which increases in the order F < Cl < Br < I.[13] The anion dependence of kinetic[6,7,9] and thermodynamic parameters for oxidative addition reactions is dramatic but there is at present no definitive explanation. For both I_2 and o-$O_2C_6Cl_4$ $-\Delta H$ is in the order NCS < N_3 which is that expected based on their total electronegativities.[61] The very low ΔH for addition of I_2 to the C_6F_5 complex may be a consequence of both an electronegativity and steric effect. For the rhodium complexes the enthalpy change for I_2 addition is in the order ($-\Delta H$) I < Br < Cl but is essentially constant for addition of o-$O_2C_6Cl_4$ as a function of halide ion.

Phosphine Dependence. The dependence of the enthalpies of oxidative addition on the neutral ligands, L, in the complexes is a function of the electronic and steric properties of the ligands. We have sought to correlate the ΔH values for I_2 and o-$O_2C_6Cl_4$ reactions with *trans*-[MCl(CO)L$_2$] with Tolman's electronic and steric parameters, ν and θ, for the tertiary phosphorus ligand. Three reactions of rhodium complexes produced unusually high heats of reaction. These were the addition of o-$O_2C_6Cl_4$ to the trimethyl phosphite (-63.1 kcal/mol) and trimethylphosphine (-61.2 kcal/mol) complexes and the reaction of the *tert*-butyldiphenylphosphine complex with iodine (-41.8 kcal/mol). These values are reproducible but appear abnormally high in comparison to the other data. We have not yet investigated these reactions in more detail and have chosen not to include them in the present correlations of ΔH values with steric and/or electronic parameters.

Plotting ΔH vs. either θ or ν revealed little correlation between the data in Table I and either the steric or electronic parameters indicating that the fit of the enthalpy data to eq 2 is poor if either A_1 or A_2 is zero. Representative coefficients

Table V. Coefficients for an Empirical Relation $-\Delta H = A_0 + A_1\theta + A_2\nu^a$ Fitted to Enthalpy Data (kcal/mol) for Oxidative Addition Reactions of Rhodium and Iridium Complexes

M	AA	A_0	A_1	A_2	A_1/A_2	f^b	R^c
Ir	I_2	−63.0	0	0.047			0.07
		75.2	−6.29	0			−0.81
		995.3	−0.425	−0.436	0.97	0.05	0.96
	o-$O_2C_6Cl_4$	71.3	−0.275	0			−0.63
		557.2	0	−0.253			−0.38
		1032.2	−0.380	0.457	0.83	0.05	0.91
	$(CN)_4C_2$	760.3	−0.368	−0.332	1.11	0.04	0.97
	SO_2	−903.1	−0.235	0.459	0.51	0.08	0.94
Rh	I_2	1293.22	−0.307	−0.592	0.52	0.10	0.85
	o-$O_2C_6Cl_4$	−246.7	−0.228	0.147	1.55	0.04	0.94

[a] θ and ν are from ref 13. [b] A value of $f < 0.1$ indicates a very good fit (see ref 62). [c] Correlation coefficient.

A_i and correlation coefficients obtained from data on reactions of iridium complexes with I_2 or o-$O_2C_6Cl_4$ are given in Table IV. A double linear regression analysis reveals a good fit of $-\Delta H$ by equations of the type 2 where both θ and ν are included. Values of A_0, A_1, and A_2 are given in Table IV for both rhodium and iridium along with correlation coefficients and the f statistic. The latter indicates a good fit between the experimental data and values calculated from the fitted equation when $f < 0.2$ and an excellent fit if $f < 0.1$.[62] These empirical relationships provide a means of calculating approximate values for heats of reaction as a function of phosphorus ligands for which ν and θ have been tabulated.[13] For example, a value of −26.9 kcal/mol is obtained for the o-$O_2C_6Cl_4$ + $IrCl(CO)(PCy_3)_2$ reaction and −16.5 kcal/mol is obtained for the analogous rhodium reaction. This would indicate that the observed heats of 0 kcal/mol are a consequence of kinetic and not thermodynamic factors. In contrast to previous findings for Lewis base addition to platinum(II) complexes[63] and the phosphine dependence of the degree of substitution in $Ni(CO)_4$ and $Ni(1,5\text{-}C_8H_{12})_2$[64] where good correlations were obtained with the steric parameter θ alone, the oxidative addition reaction is sensitive to both steric and electronic effects.

Comparison of A_1 and A_2, coefficients of θ and ν, respectively, or the ratios A_1/A_2 (Table V) for the reactions studied does not reveal any clear trends. The reaction of o-$O_2C_6Cl_4$ or TCNE with the iridium(I) complexes would be expected to be particularly sensitive to the steric effects of the phosphine ligands since the latter become cis in the iridium(III) products and the added ligands are the largest studied. However, the coefficients, A_1, for these reactions are not very much above the average value. The equations in Table V provide a means of calculating ΔH from ν and θ values but the potential of this approach in quantifying steric and electronic effects on thermodynamic parameters must be left open to question until more reactions are studied.

The triphenylarsine complexes of iridium and rhodium react with greater heat evolution than their triphenylphosphine analogues. The greater reactivity of tertiary arsine complexes has been discussed by Shaw.[65]

Effect of CS in *trans*-[MCl(CS)(PPh$_3$)$_2$]. The complex *trans*-$[IrCl(CS)PPh_3)_2]$ has been found to be less reactive than Vaska's complex in oxidative addition reactions, and evidence indicates that CS is a stronger π acceptor than CO.[66] For example, the reaction with CH_3I is immeasurably slow and the complex reacts more slowly with TCNE[48] than the CO analogue. For M = Ir both I_2 and o-$O_2C_6Cl_4$ react more exothermically with the CS than the CO complex but for the rhodium complexes the heats are slightly lower for the thiocarbonyl analogue. This reversal in trends may indicate that the differences in electron donor and acceptor properties of the carbonyl and thiocarbonyl ligands are small enough to be counterbalanced by other factors in the complex.

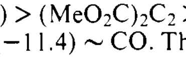
Approximation of *D*(Ir–X) for the Halogens. Vaska[23] has suggested a procedure for approximating Ir–X bond energies using enthalpies of oxidative addition reactions of a diatomic molecule, X_2, to *trans*-$[IrCl(CO)(PPh_3)_2]$ and applied it to calculation of an approximate bond energy $D_A(\text{Ir–H}) = 59.5$ kcal/mol. In summary the equation he derived for the approximation is similar to the following except that we have included solvation terms.

$$2D_A(\text{Ir–X}) \approx D(\text{X–X}) - \Delta H_{\text{meas}} + \Delta H_{\text{solvX}_2} + \Delta H_r - \Delta H_{\text{solv,Ir(I)}} + \Delta H_{\text{solv,Ir(III)}} \quad (4)$$

The terms $\Delta H_{\text{solvX}_2}$ and ΔH_r are the heats of solvent-X_2 interaction and the enthalpy of rehybridization for the square planar to octahedral change in geometry which occurs. The other terms are those discussed in eq 3. The term ΔH_r is not experimentally accessible so it is included in the calculated $D_A(\text{Ir–X})$. The values of $D(\text{X–X})$[67] are from the literature.

For the term $\Delta H_{\text{solvX}_2}$ the heat of the C_6H_6–I_2 interaction and mean molar heat of solution of Cl_2 in C_6H_6 (−3.20 kcal/mol)[68] have been used. The heat of solution of Br_2 was approximated by using the average of these two numbers. The remaining solvation terms are assumed to be of similar magnitude and to add to near zero. Calculated values of $D_A(\text{Ir–X})$ for the halogens are given in Table III. It is encouraging that the enthalpies for the addition of HCl and HBr to *trans*-$[IrClCO(PPh_3)_2]$ calculated using $D_A(\text{Ir–X})$ and heats of solution in benzene for HCl (−5.7 kcal/mol)[69] and HBr (−4.2 kcal/mol),[70] −21 and −22 kcal/mol, respectively, are in good agreement with the experimental values (−21.0 ± 1.0 and −26.0 ± 2.0 kcal/mol). The calculated $D_A(\text{Ir–I})$ values are significantly influenced by the nature of the phosphorus ligand and span a range of 39.5 ± 1.5 (PMe_2Ph) to 32.1 ± 1.2 kcal/mol (PCy_3).

In summary, from the present results and those from previous studies already cited, enthalpy changes for oxidative additions to *trans*-$[IrCl(CO)(PPh_3)_2]$ became less exothermic in the following order: $Cl_2 > Br_2\ (-59) > I_2 > o\text{-}O_2C_6Cl_4\ (-28.9) > HBr > HCl > (CF_3)_2C_2 > C_2(CN)_4\ (-19.9) > O_2 > C_2F_4 > H_2\ (-15.0) > (MeO_2C)_2C_2 > cis\text{-}(MeO_2C)_2(CH)_2 > C_2H_4 > \text{i} > SO_2\ (-11.4) \sim CO$. The ΔH values in parentheses provide a scale for comparison. Approximate bond energies, $D_A(\text{Ir–X})$, decrease in the series Cl > H > Br > I. The success in fitting ΔH data for oxidative addition reactions to eq 2 allows the calculation of enthalpies for reaction of complexes of any phosphorus ligand included in Tolman's extensive compilation of ν and θ values. The lack of discernible trends in the magnitude of the coefficients of ν and θ in eq 2 requires further study. Such trends might become apparent



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as more systems are studied. If not, it may be that steric effects are minimized by the intermeshing of ligands that has recently been discussed by Clark.[71] Our success in calculating values of ΔH for addition of HCl and HBr to *trans*-[IrCl(CO)(PPh$_3$)$_2$] in good agreement with experimental results using the D_A(Ir–X) values suggests that this approach might be extended to other ligands.

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Supplementary Material Available: Equilibrium constants and enthalpies for reactions of dimethyl acetylenedicarboxylate (9 pages). Ordering information is given on any current masthead page.

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