observed, (ii) the increase in *fac* WFF on shorter wavelength excitation, and (iii) the observation of an increase in *mer* WFF/*mer* FWF at shorter wavelength. The theory therefore provides a satisfactory qualitative rationalization of the data. There are too many uncertainties to pursue a quantitative analysis.

It is unfortunate that no information is available on the extent of axial vs. equatorial ammonia loss and its wavelength dependence, as this would facilitate a clearer analysis and a better test of the theory. Nevertheless the theory accounts better for the data than the edge displacement model, most notably in explaining the small yields of *fac* WFF. The latter observation is the only one to date that provides any real evidence for the importance of symmetry restrictions over and above the constraints imposed by the original edge displacement proposal.

A further major aspect of the observations has been neglected till now. Attention was drawn to the equivalency of the excited-state tbp intermediates derived from the lowest quartet states of *trans*- and *cis*-$[Cr(NH_3)_4F_2]^+$ via which the major proportion of the photochemistries appears to occur. This tbp intermediate leads to *mer* WFF from its excited state and *mer* FWF from its ground state. Only if it is allowed that reaction can occur to differing extents from the electronically excited and ground states of this tbp intermediate for the two systems is it possible to explain the differing meridional isomer ratios. If not, or if it is required that these two states be in Boltzmann equilibrium prior to reaction, then a problem exists for the VC theory. Further if reaction via only the ground state of the tbp intermediate is expected, then only *mer* WFF would be produced. It seems that our data absolutely requires, in the context of the VC theory, reaction via electronically excited intermediates together with ground state and that, for some reason, the ratio of excited- to ground-state reaction may depend on the origin of the tbp intermediate species.

The superiority of the VC theory over the edge displacement model should not be interpreted as supporting a dissociative model for Cr(III) photochemistry. It may well be that the steric course of the reaction is predisposed by the symmetry requirements for an idealized five-coordinate process, but it remains very likely that both the leaving group and entering group are simultaneously in the picture, and this offers other mechanisms to explain differing product ratios from the lowest quartet reactions of the cis and trans complexes. There is some experimental evidence to show that Cr(III) photoreactions may be associative.[29] The VC theory should be considered a useful technique rather than a picture of reality.

In summary, it has been shown that ammonia photoaquation from *trans*-$[Cr(NH_3)_4F_2]^+$ is stereomobile, that the stereochemistry of photolysis of this complex is consistent with both the edge displacement model and the VC theory, that the cis complex photostereochemistry provides the first evidence of the operation of the VC type symmetry rules, and that, by accepting the participation of both $^4B_2$ and $^4E$ excited states in photochemistry, the VC model gives a reasonably good account of the photochemical reaction modes and stereochemistries of both molecules. Since the same intermediate is involved in the major mode for the two complexes, the different photochemistries emphasize that the mechanism is unlikely to be truly dissociative.

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**Registry No.** *trans*-$[Cr(NH_3)_4F_2]^+$, 31253-66-4; *cis*-$[Cr(NH_3)_4F_2]^+$, 58864-86-1; *mer* FWF, 75010-87-6; *mer* WFF, 75045-11-3; *fac* WFF, 75045-12-4.

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# Enthalpy Changes in Oxidative Addition Reactions of Organic Iodides with *trans*-Chlorocarbonylbis(trimethylphosphine)iridium(I)

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Titration calorimetric methods have been used to determine enthalpies of the oxidative addition reaction of *trans*-$[IrCl(CO)(PMe_3)_2]$ with $I_2$, HI, $CH_3I$, $C_2H_5I$, *n*-$C_3H_7I$, *i*-$C_3H_7I$, $C_6H_5CH_2I$, $CH_3C(O)I$, and $C_6H_5C(O)I$ in 1,2-dichloroethane. Heats of solution of selected metal complexes and iodo compounds have been determined. These results were used to calculate $\Delta H°$ values for the oxidative addition reactions. Combination of the $\Delta H°$ values and heats of formation of the appropriate compounds has made it possible to calculate $\Delta H°$ for the $\beta$-elimination reaction of an ethyl complex, CO insertion into the Ir–$CH_3$ bond, and the isomerization of an isopropyl to an *n*-propyl complex. A relative scale of bond energies, $D(Ir–R) - D_1(Ir–I)$ has been determined based on the data obtained in this study. The general trend in $D(Ir–R)$ is $H > CH_3 \approx I \approx CH_3C(O) > C_2H_5 > n\text{-}C_3H_7 > i\text{-}C_3H_7 > CH_2C_6H_5$.

To date, no thermochemical information has been available concerning the oxidative addition reaction of organic halides with $d^8$ metal centers. Kinetic, synthetic, and structural studies have made reactions of the Vaska-type complexes *trans*-$[IrCl(CO)L_2]$ (L = tertiary phosphine), the best characterized model system for this class of reactions.[1-9] In general, the oxidative addition reaction has been very important in the development of organometallic chemistry since it is widely encountered in stoichiometric or catalytic syntheses which are mediated by transition-metal complexes.[2,4,5] Thermochemical

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information will add a new dimension to the understanding of this important class of reactions.

We have discussed available thermochemical information for reactions of iridium(I) and rhodium(I) complexes in a recent paper reporting application of titration calorimetry to the thermochemical study of this reaction type.[10] Other work to date has primarily involved reactions in which the added molecules remain intact, e.g., olefins, acetylenes, dioxygen, sulfur dioxide, and a few other unsaturated compounds. This is true for complexes of the Vaska type, *trans*-$[IrCl(CO)L_2]$ (L = a tertiary phosphine) (see ref 10 and references therein), which has been the primary model for $d^8$ systems and for $Pt(PPh_3)_2(C_2H_4)$ which has been the primary model for $d^{10}$ systems.[11,12] Thermochemical information for oxidative addition involving bond cleavage in the added molecule has been limited to reaction of dihydrogen,[13,14] dihalogens, and hydrogen halides with the Vaska-type system[10,15] and $CH_3I$ with the platinum(0) system.[16] As we shall illustrate, data for addition of organic halides can be used to obtain approximations of metal–ligand bond enthalpy contributions and to calculate enthalpy changes for important organometallic transformations (e.g., CO insertion and $\beta$-elimination reactions). Application of the data to the approximation of a relative scale of metal–ligand bond enthalpy contributions is of particular value since other thermochemical methods[17,18] are not readily adaptable to the study of these highly substituted complexes.

## Experimental Section

Acetyl iodide,[19] benzoyl iodide,[20] benzyl iodide,[19] and *trans*-$[IrCl(CO)(PMe_3)_2]$[21] were prepared by methods in the literature. The iridium complex was stored in sealed ampules each of which contained enough sample for one experiment. Methyl, ethyl, *n*-propyl, and isopropyl iodides (Aldrich) were distilled prior to use and stored for short periods over copper turnings at 0 °C. Diiodine (Baker) was used as received. Hydrogen iodide (Air Products) was transferred in vacuo to the reaction vessel. Benzene was distilled and stored over molecular sieves, and 1,2-dichloroethane was distilled from $P_4O_{10}$ prior to use. Infrared spectra was recorded on a Perkin-Elmer Model 621 spectrometer, and $^1H$ NMR spectra were obtained by using a Varian T60 spectrometer.

**Calorimetry.** The Tronac 450-4 titration calorimeter has been previously described.[10] In general 0.02–0.08 g of the iridium complex was placed in a 2-mL volumetric flask. The flask was purged with $N_2$ for 25–30 min, and then solvent, purged with $N_2$, was added to the mark and the solution transferred to the titration buret under a slow stream of $N_2$. If the compound to be reacted with the metal complex was a solid, it was placed in the reaction vessel which was then purged with argon for 25–30 min. Solvent, 40 mL, was added via syringe through a Teflon delivery line. If the addend was a liquid, it was degassed with $N_2$ for 20–30 min and a known amount added via syringe to the reaction dewar which had been previously purged with argon for 25–30 min, and then enough solvent was added via syringe to give a total volume of 40 mL. Enthalpy changes were measured by using standard techniques.[22] Usually a series of aliquots of the metal complex solution ($\approx 5 \times 10^{-2}$ M) were added via buret to a solution of the halide (0.05–0.5 M), and the heat changes for each addition were evaluated. These were found to be independent of concentration of reactants in the range studied. The titration curves and heat data were indicative of reactions having $K > 10^4$, so $\Delta H$ values were obtained directly from the experimental heat values. This data for the series of iodo compounds is given in Table I. Each value is the average of between 6 and 20 determinations on at least two independently prepared samples of complex and iodo compound. In some cases we applied the least-squares method of Drago[23] to calculate $K$ and $\Delta H$, but since $K$ was so large, the method provided no advantage. Care was taken not to contact acetyl iodide, hydrogen iodide, or benzoyl iodide with metal surfaces because this was found to promote formation of $I_2$. Due to formation of free $I_2$ in the presence of air, both acetyl iodide and HI were condensed in vacuo and then transferred in vacuo from a trap (<0 °C to prevent sublimation of $I_2$) into 40 mL of degassed solvent. The degassed solution was then transferred under a flow of argon into the calorimeter dewar which had been previously purged with argon. Even these precautions did not allow complete exclusion of $I_2$. However, $I_2$ was found to react with *trans*-$[IrCl(CO)(PMe_3)_2]$ faster than either HI or acetyl iodide. With titration of the solution with metal complex until all the free $I_2$ was consumed, a constant enthalpy value for the desired reaction could be obtained.

Table I. Enthalpy Changes (kJ $mol^{-1}$) for Oxidative Addition Reactions in 1,2-Dichloroethane ($\Delta H$) and the Standard State ($\Delta H°$)

| | $-\Delta H^a$ | $-\Delta H°\ ^c$ |
|---|---|---|
| $I_2$ | 185.4 ± 7.1 | 164.0 ± 7.9 |
| HI | 160.2 ± 2.9 | |
| | 167.8 ± 2.9[b] | 188 ± 13 |
| $CH_3I$ | 117.2 ± 6.7 | 117.6 ± 7.9 |
| $C_2H_5I$ | 109.6 ± 2.9 | 107.1 ± 5.0 |
| 1-$C_3H_7I$ | 102.9 ± 3.8 | 102.1 ± 5.9 |
| 2-$C_3H_7I$ | 88.3 ± 9.6 | 88.3 ± 9.6 |
| $C_6H_5CH_2I$ | 94.9 ± 6.7 | 94.9 ± 6.7 |
| $CH_3C(O)I$ | 125.5 ± 4.2 | 125.5 ± 4.2 |
| $C_6H_5C(O)I$ | 121.3 ± 3.3 | 121.3 ± 3.3 |

[a] Error limits are one standard deviation. [b] In $C_6H_6$. [c] Error limits are $(\Sigma_{i=1}\sigma_i^2)^{1/2}$.

Table II. Enthalpies of Solution, $\Delta H_{soln}$, and Vaporization, $\Delta H_{vap}$, for Selected Metal Complexes and Iodo Compounds

| | $\Delta H_{soln}$,[a] kJ $mol^{-1}$ | | $\Delta H_{vap}$,[c] kJ $mol^{-1}$ |
|---|---|---|---|
| | R–X | IrCl(CO)·$(PMe_3)_2$·RI | R–X |
| *trans*-$\{IrCl(CO)[P(CH_3)_3]_2\}$ | | 17.1 ± 4.1 | |
| $I_2$ | 23.1 ± 0.5 | 18.1 ± 1.0 | 62.4 ± 0.1 |
| $CH_3I$ | 1.09 ± 0.04 | 18.6 ± 0.4 | 28.1 ± 1.3 |
| $C_2H_5I$ | 1.55 ± 0.13 | 15.9 ± 0.8 | 31.8 ± 0.08 |
| *n*-$C_3H_7I$ | 1.51 ± 0.04 | 18.0 ± 0.8 | 35.9 ± 0.1 |
| H–I | −20.9[b] | | |
| $CH_3C(O)Cl$ | 0.21 ± 0.04 | | |

[a] Error limits are one standard deviation. [b] In $C_6H_6$. Approximated by the mean of the HCl and HBr values from ref 30.
[c] See ref 32.

Heats of solution of liquid compounds were measured by adding a known amount of the liquid to 40 mL of the solvent via the buret. For measurement of heats of solution for solid compounds, a known amount of the solid to be studied was sealed in a glass ampule. Then the ampule was placed in an ampule-breaking apparatus which was fitted into the reaction dewar. Heats of solution of *trans*-$[IrCl(CO)(PMe_3)_2]$, of its $I_2$, $CH_3I$, $C_2H_5I$, and *n*-$C_3H_5I$ adducts and of $CH_3I$, $I_2$, $C_2H_5I$, *n*-$C_3H_7I$, and $CH_3C(O)Cl$ in the solvent 1,2-$C_2H_4Cl_2$ were measured in this way and are given in Table II. The heat of solution of acetyl chloride was determined as an approximation of that for acetyl iodide.

The standard resistance heater was calibrated periodically by using the 0.1 N HCl–(tris(hydroxymethyl)amino)methane titration. The observed $\Delta H$ was −47.3 ± 2.5 kJ/mol (lit.[22] −47.79 kJ/mol). To check

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the ampule-breaking system, we determined the heat of solution of potassium chloride: found −17.03 ± 0.54 kJ/mol (lit.[24] 17.51 kJ/mol).

Upon completion of a calorimeter run the reaction solution was evaporated to dryness in vacuo and the $^1H$ NMR and IR spectra of the residue were obtained. The spectroscopic values were identical with those of authentic samples prepared by reacting the iridium(I) complex with the iodo compound. Except as noted below, only one product was present. In the case of HI, $CH_3C(O)I$, and $C_6H_5C(O)I$, the residue contained some $I_2$ adduct as an impurity which was formed during the preliminary additions of metal complex used to scavenge the adventitious $I_2$.

Spectral and physical properties of the complexes are as follows.

$IrCl(CO)(PMe_3)_2{\cdot}I_2$: orange solid, mp 120 °C dec; IR (Nujol) 2040, 2026, ($IrC{\equiv}O$), 302 (Ir–Cl) $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.98 (t, $PCH_3$).

$IrCl(CO)(PMe_3)_2{\cdot}CH_3C(O)I$: IR (Nujol) 2043 ($IrC{\equiv}O$), 1619 ($CH_3C{=}O$), 305 (Ir–Cl) $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 2.11 (t, $PCH_3$), 2.32 (s, $CH_3CO$).

$IrCl(CO)(PMe_3)_2{\cdot}HI$: Ir (Nujol) 2159 (Ir–H), 2027 ($IrC{\equiv}O$), 295 (IrCl) $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 2.13 (t, $PCH_3$).

$IrCl(CO)(PMe_3)_2{\cdot}CH_3I$: cream color, mp 165 °C dec; IR (Nujol) 2028 (lit.[9] 2024) ($C{\equiv}O$), 299 (lit. 299) (Ir–Cl) $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.83 (lit.[9] 1.82) (t, $PCH_3$), 0.89 (lit.[9] 0.85) (s, $IrCH_3$).

$IrCl(CO)(PMe_3)_2{\cdot}C_2H_5I$: cream color, mp 150 °C dec; IR (Nujol) 2032, 2016 (lit.[9] 2021) ($C{\equiv}O$), 297 (lit.[9] 304) (Ir–Cl) $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.87 (lit.[9] 1.87) (t, $PCH_3$), 1.48 (t, $CH_3CH_2$), 1.00 (m, $CH_2$).

$IrCl(CO)(PMe_3)_2{\cdot}n\text{-}C_3H_7I$: colorless, mp 120–121 °C dec; IR (Nujol) 2024 and 2002 ($C{\equiv}O$), 311 (Ir–Cl) $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.85 (t, $PCH_3$), 1.00 (t, $CH_3$), 1.27 (m, $CH_2CH_3$).

$IrCl(CO)(PMe_3)_2{\cdot}i\text{-}C_3H_7$: tan, mp 125 °C dec; IR (Nujol) 2008, 2020 (lit.[9] 2010, 2028) ($C{\equiv}O$), 311 (lit.[9] 311) (Ir–Cl) $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.92 (lit.[9] 1.93) (t, $PCH_3$), 1.40 (lit.[9] 1.44) (d, $CH_3$), 2.94 (lit.[9] 2.96) (m, CH).

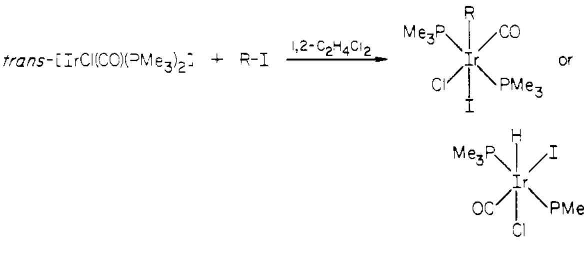
$IrCl(CO)(PMe_3)_2{\cdot}C_6H_5CH_2I$: cream color; IR (Nujol) 2029 ($C{\equiv}O$).

$IrCl(CO)(PMe_3)_2{\cdot}C_6H_5C(O)I$: colorless, mp 110 °C dec; IR (Nujol) 2039, 2006 ($C{\equiv}O$), 1630, 1599, 1584, and 1570 $cm^{-1}$ ($C{=}O$), 302 (Ir–Cl) $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.75 (t, $PCH_3$), 7.4 (m, $C_6H_5$).

## Results

In order to use adiabatic titration calorimetric methods to study the oxidative addition process, we have found that reactions should reach equilibrium in less than 10–15 min. In order to obtain results on as wide a range of organic halides as possible, we have chosen the very reactive complex *trans*-$[IrCl(CO)(PMe_3)_2]$ as our reference metal complex. Even with this complex only organic iodides, in general, react rapidly enough for study. Chlorides and bromides have usually been found to react much more slowly.[9,26]

The reaction system we have studied is given in eq 1 (R =



(1)

I, H, $CH_3$, $C_2H_5$, $n$-$C_3H_7$, $i$-$C_3H_7$, $CH_3C(O)$, $C_6H_5C(O)$, or $CH_2C_6H_5$). Numerous studies of the stereochemistry of reaction of these and/or similar halo compounds with complexes of the Vaska type have been reported.[9,26–28] The pattern for compounds of the type in eq 1 is as shown. Labinger[9] and Bennett[29] have characterized many of the adducts of addition of organic halides to the $PMe_3$ complex. We have characterized each reaction mixture by $^1H$ NMR and IR spectroscopy. Our data, given in the Experimental Section, is consistent with the results of previous work, establishes that the stereochemistry is as shown, and establishes that within the limits of detection only one product is formed in each reaction under the conditions studied (short reaction times, 25 °C, in darkness).

## Discussion

The observed enthalpy changes for the oxidative addition reaction of iodo compounds, R–I, in ethylene dichloride can be written as a composite of the terms given in eq 2. The bond

$$\Delta H_{RI} = D(R{-}I) - D(Ir{-}R) - D_2(Ir{-}I) + \Delta H_{soln,Ir{\cdot}RI} - \Delta H_{soln,Ir} - \Delta H_{soln,RI} - \Delta H_{sub,Ir{\cdot}RI} + \Delta H_{sub,Ir} + \Delta H_{vap,RI} \quad (2)$$

dissociation energy terms, $D$, are those of the iodo compounds in Table I, the $(PMe_3)_2(CO)ClIIr{-}R$ bond and the iridium–iodine bond in $(PMe_3)_2(CO)ClIr{-}I$, respectively. The remaining terms are the enthalpies of dissolving solid *trans*-$[IrCl(CO)(PMe_3)_2]$ (abbreviated Ir) and its RI adduct (abbreviated Ir·RI) in ethylene dichloride, the enthalpies of sublimation of these two metal complexes, the heat of dissolving the iodo compound in 1,2-dichloroethane, $\Delta H_{soln,RI}$, and the heat of vaporization of RI. A number of experiments have been carried out to assess the contributions of these terms. We have determined the enthalpies of solution for the iridium(I) complex and representative adducts with iodo compounds and pure organic iodides. The data are given in Table II. Acetyl iodide proved difficult to work with, so we have measured the heat of solution of acetyl chloride as an approximation and assume the value is similarly small. The heats of solution of the organic halides are small relative to the experimental error in the heats of reaction (Table I). Only diiodine is an exception to this. Within experimental error the heats of solution of the iridium(I) complex and its adducts with organic halides are the same. These observations are reflected in the standard enthalpies of reaction, $\Delta H_{RI}°$, given in Table I which refer to (R–I in its standard state) eq 3. For the organic halides,

$$trans\text{-}[IrCl(CO)(PMe_3)_2](s) + R{-}I \rightarrow [(PMe_3)_2(CO)ClIr{\cdot}RI](s) \quad (3)$$

within experimental error, $\Delta H_{RI}° \approx \Delta H_{RI}$ for the solution phase reaction for methyl, ethyl, and $n$-propyl iodide. We have assumed the same is true for the other organic groups used in this study. For hydrogen iodide, no heat of solution value is available. In order to approximate the standard heat of the oxidative reaction of HI, we have measured the reaction heat in benzene and used the mean of the known heats of solution of HCl and HBr in benzene[30] as the heat of solution for HI, −20.9 kJ/mol. This is likely to be within ±12.5 kJ of the true value.

A goal of our work has been to obtain information about the iridium–ligand bond energy terms in eq 2. Expressing these in terms of the $\Delta H°$ values for RI addition that we have just discussed gives eq 4. The two iridium bond energy terms

$$D(Ir{-}R) + D_2(Ir{-}I) = \Delta H_{RI}° + D(R{-}I) - \Delta H_{sub,Ir{\cdot}RI} + \Delta H_{sub,Ir} + \Delta H_{vap,RI} \quad (4)$$

cannot be determined independently so we have adopted the approach previously used by Mortimer et al.[15] in their work on the thermochemistry of $CH_3I$ addition to platinum(0)

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**Table III.** Approximated Values of *D*(Ir–R) Relative to $D_1$(Ir–I) (kJ mol$^{-1}$)

| R | $D(\mathrm{Ir{-}R}) - D_1(\mathrm{Ir{-}I})^a$ | R | $D(\mathrm{Ir{-}R}) - D_1(\mathrm{Ir{-}I})^a$ |
|---|---|---|---|
| H | 59 ± 12 | *i*-$C_3H_7$ | −31.0 ± 15.5 |
| $CH_3$ | 2 ± 13 | $C_6H_5CH_2$ | −69.5 ± 15.6 |
| $C_2H_5$ | −15.9 ± 11.7 | $CH_3C(O)$ | −3 ± 16 |
| *n*-$C_3H_7$ | −14.2 ± 13.0 | | |

[a] Error limits are $(\Sigma_{i=1}\sigma_i^2)^{1/2}$.

compounds. An expression for the difference, *D*(Ir–R) − $D_1$(Ir–I), is obtained by subtracting data for the $I_2$ reaction from that for the RI reaction (eq 5). The first two terms are

$$D(\mathrm{Ir{-}R}) - D_1(\mathrm{Ir{-}I}) = \Delta H_{\mathrm{I}_2}^\circ - \Delta H_{\mathrm{RI}}^\circ + D(\mathrm{R{-}I}) - D(\mathrm{I{-}I}) + \Delta H_{\mathrm{vap,RI}} - \Delta H_{\mathrm{sub,I_2}} + \Delta H_{\mathrm{sub,Ir\cdot I_2}} - \Delta H_{\mathrm{sub,Ir\cdot RI}} \qquad (5)$$

available from our work and the next four are available in the literature.[31,32]

At present, data are not available for heats of sublimation of any tertiary phosphine complexes of iridium. Other workers studying the thermochemistry of iridium and platinum complexes have made the assumption that the difference between the heat of sublimation of the reactant and product metal complexes is approximately zero. This has been discussed by Mortimer and co-workers[11,33,34] and by Brown and co-workers.[35] Mortimer et al.[16] made the same approximation in their Pt(0)–$CH_3I$ work. Halpern and co-workers[36] made similar assumptions in approximating *D*[Co–CH($CH_3$)(Ph)].

Making the assumption that the heats of sublimation terms for the metal complexes in eq 5 are approximately equal allows the set of *D*(Ir–R) − $D_1$(Ir–I) values in Table III to be calculated. The trend in *D*(Ir–R) suggests that within the limits of the approximation that bond energies fall into three groups in the order H > $CH_3 \approx$ I $\approx CH_3C(O) \approx$ *n*-$C_3H_7 \approx C_2H_5 \approx$ *i*-$C_3H_7$ > $C_6H_5CH_2$. It is interesting that the trend found in the Ir–C bond energies as a function of R is the same as that found for *D*(R–H)[31] and *D*(R–I).[31] This has also been observed for Hg–C bonds.[37]

Vaska and Werneke[13] obtained an approximate value of the mean iridium–hydrogen bond energy, $\bar{D}$(Ir–H) ≃ 251 kJ, from data on reaction 6. To do so they assumed the heats of

$$\textit{trans}\text{-}[\mathrm{IrCl(CO)(PPh_3)_2}] + \mathrm{H_2} = \mathrm{IrClH_2(CO)(PPh_3)_2} \qquad \Delta H = -63\ \mathrm{kJ/mol} \qquad (6)$$

sublimation and of solution of the reactant and product complexes were equal and canceled out of an equation analogous to eq 2. Our data for diiodine, by the same procedure, yields a value of $\bar{D}$(Ir–I) = 189.5 ± 7.5 kJ/mol. This comparison of the approximate mean bond dissociation energies provides an independent determination of a 63 kJ difference between Ir–H and Ir–I bond energies.

The $\Delta H°$ values in Table I can be used in combination with $\Delta H_f°$ for organic compounds to calculate $\Delta H°$ for three reactions of wide importance in organometallic chemistry. The enthalpy change for the isomerization of the isopropyl to the *n*-propyl iridium complex, eq 7d, is the sum of the $\Delta H$ values for eq 7a–c (Ir ≡ IrCl(CO)($PMe_3$)$_2$). The small enthalpy change for this isomerization process indicates that small changes in the environment of the propyl group can influence the position of equilibrium. That was found by Bennett et al.,[38] who reported that in the $PMe_2Ph$ analogue of our system the isopropyl complex isomerizes completely and rapidly to the normal isomer in polar solvents but a less sterically crowded complex $[C_3H_7IrCl_2(CO)_2]_2$ reaches an equilibrium having a ratio of 2:3 of isopropyl to *n*-propyl forms.

$$\mathrm{I{-}Ir{-}CH(CH_3)_2(s) = Ir(s) + I{-}CH(CH_3)_2(l)} \qquad \Delta H° = +88.3 \pm 9.6\ \mathrm{kJ/mol} \qquad (7a)$$

$$\mathrm{I{-}CH_2CH_2CH_3(l) + Ir(s) = I{-}Ir{-}CH_2CH_2CH_3(s)} \qquad \Delta H° = -102.1 \pm 5.9\ \mathrm{kJ/mol} \qquad (7b)$$

$$\mathrm{ICH(CH_3)_2(l) = ICH_2CH_2CH_3(l)} \qquad \Delta H° = +9.2 \pm 13.8\ \mathrm{kJ/mol} \qquad (7c)$$

$$\mathrm{I{-}IrCH(CH_3)_2(s) = I{-}IrCH_2CH_2CH_3(s)} \qquad \Delta H° = -5 \pm 29\ \mathrm{kJ/mol} \qquad (7d)$$

The $\Delta H$ for CO insertion into the Ir–$CH_3$ bond, eq 8d, can

$$\mathrm{I{-}Ir{-}CH_3(s) \rightarrow CH_3I(l) + Ir(s)} \qquad \Delta H = 117.6 \pm 7.9\ \mathrm{kJ/mol} \qquad (8a)$$

$$\mathrm{Ir(s) + CH_3C({=}O){-}I(l) \rightarrow I{-}Ir{-}C({=}O){-}CH_3(s)} \qquad \Delta H = -125.5 \pm 4.2\ \mathrm{kJ/mol} \qquad (8b)$$

$$\mathrm{CH_3I(l) + CO(g) \rightarrow CH_3C({=}O){-}I(l)} \qquad \Delta H = -38.9 \pm 2.1\ \mathrm{kJ/mol} \qquad (8c)$$

$$\mathrm{I{-}Ir{-}CH_3(s) + CO(g) \rightarrow Ir{-}C({=}O){-}CH_3(s)} \qquad \Delta H = -46.8 \pm 14.2\ \mathrm{kJ/mol} \qquad (8d)$$

be obtained as follows. The net reaction can be written as the sum of reactions 8a–c. The $\Delta H$ for 8c is derived from heats of formation for the substances[32] (Ir = IrCl(CO)($PMe_3$)$_2$). The value of $\Delta H$ is not large, which is as would be anticipated for a reaction found to be reversible in a wide range of systems.[39] Since our data indicate *D*(Ir–$CH_3$) and *D*(Ir–C(O)$CH_3$) are nearly equal, the driving force for the CO insertion reaction is apparently the formation of the new carbon–carbon bond.

In a similar way the $\Delta H$ for the $\beta$-elimination reaction, eq 9d, of the iridium(III) ethyl complex can be written as the sum of eq 9a–c. The overall process is endothermic in this case.

$$\mathrm{I{-}IrC_2H_5(s) \rightarrow Ir(s) + C_2H_5I(l)} \qquad \Delta H = 107.1 \pm 5.0\ \mathrm{kJ/mol} \qquad (9a)$$

$$\mathrm{Ir(s) + HI(g) \rightarrow I{-}Ir{-}H(s)} \qquad \Delta H = -188 \pm 13\ \mathrm{kJ/mol} \qquad (9b)$$

$$\mathrm{C_2H_5I(l) \rightarrow C_2H_4(g) + HI(g)} \qquad \Delta H = 118.8 \pm 2.9\ \mathrm{kJ/mol} \qquad (9c)$$

$$\mathrm{I{-}Ir{-}C_2H_5(s) \rightarrow I{-}Ir{-}H(s) + C_2H_4(g)} \qquad \Delta H_{\mathrm{calcd}} = 38 \pm 20\ \mathrm{kJ/mol} \qquad (9d)$$

On the basis of enthalpy considerations, these results imply that acyl and alkyl complexes should be more stable than the corresponding products of the elimination reactions. Observations of chemical behavior bear this out. Numerous coordinatively saturated iridium(III) acyls[26,27,40,41] and alkyls have

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been characterized. Six-coordinated acyls of the type $IrCl_2[C(O)R](CO)L_2$ are quite stable, though they can be decarbonylated by heating in an open system where carbon monoxide is lost. The reverse process, CO insertion, occurs at mild temperatures and low pressures of CO or in the presence of added nucleophiles.[40–42] Insertion of olefins into iridium–hydrogen bonds has also been observed under mild conditions.[43]

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**Registry No.** *trans*-$[IrCl(CO)(PMe_3)_2]$, 21209-86-9; $IrCl(CO)(PMe_3)_2 \cdot I_2$, 75112-06-0; $IrCl(CO)(PMe_3)_2 \cdot CH_3C(O)I$, 75125-15-4; $IrCl(CO)(PMe_3)_2 \cdot HI$, 75112-07-1; $IrCl(CO)(PMe_3)_2 \cdot CH_3I$, 74524-96-2; $IrCl(CO)(PMe_3)_2 \cdot C_2H_5I$, 74511-76-5; $IrCl(CO)(PMe_3)_2 \cdot n\text{-}C_3H_7I$, 75112-08-2; $IrCl(CO)(PMe_3)_2 \cdot i\text{-}C_3H_7I$, 74511-77-6; $IrCl(CO)(PMe_3)_2 \cdot C_6H_5CH_2I$, 75112-09-3; $IrCl(CO)(PMe_3)_2 \cdot C_6H_5C(O)I$, 75112-10-6; $I_2$, 7553-56-2; HI, 10034-85-2; $CH_3I$, 74-88-4; $C_2H_5I$, 75-03-6; 1-$C_3H_7I$, 107-08-4; 2-$C_3H_7I$, 75-30-9; $C_6H_5CH_2I$, 620-05-3; $CH_3C(O)I$, 507-02-8; $C_6H_5C(O)I$, 618-38-2; $CH_3C(O)Cl$, 75-36-5.

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# Nucleophilic Displacement of the Chelating Bis(sulfoxide) from *cis*-[*meso*-1,2-Bis(phenylsulfinyl)ethane]dichloroplatinum(II) and *cis*-[*rac*-1,2-Bis(phenylsulfinyl)ethane]dichloroplatinum(II)

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The kinetics of ring opening, by amines in 1,2-dimethoxyethane, have been measured for two bis(sulfoxide)–platinum(II) isomers. The results make possible a discussion of the differences between the two isomers, in comparison with other platinum(II) complexes, in terms of absolute reactivity, nucleophilic discrimination, and steric retardation effects.

## Introduction

Kinetic studies of the closing and opening of chelate rings in 4-coordinated square-planar $d^8$ complexes as a means of investigating the chelate effect in systems that undergo associatively activated substitution have become of increasing interest in recent years. Much of the work has been done with chelating polyamines[2] where control of the process can be obtained by a suitable choice of pH and is therefore restricted to aqueous solutions. The other studies in this area were, until now, restricted to ring opening and subsequent displacement of chelating bis(thioethers)[3] and bis(selenoethers)[4] by amines in dimethoxyethane solutions.

We have recently synthesized and characterized[5] meso and racemic isomers of [1,2-bis(phenylsulfinyl)ethane]dichloroplatinum(II), whose structures are shown in Figure 1, and now wish to report the kinetics of the displacement of the chelating bis(sulfoxides) from platinum in order (a) to compare the behavior of sulfoxides with thioethers and (b) to examine the extent to which the reactivity depends upon the isomeric form.

## Experimental Section

**Materials.** [*meso*-1,2-Bis(phenylsulfinyl)ethane]dichloroplatinum(II) and [*rac*-1,2-bis(phenylsulfinyl)ethane]dichloroplatinum(II) were prepared and purified by previously reported methods.[5] The amines, with the exception of 4-chloropyridine, were purified by distillation over KOH pellets at reduced pressure under an atmosphere of nitrogen. 4-Chloropyridine, which decomposes by this treatment, was obtained from the hydrochloride which was dissolved in water and treated with an excess of $Na_2CO_3$. The amine was extracted with diethyl ether, the extract dried over $Na_2SO_4$, and the pure amine separated by distillation under a reduced pressure of nitrogen. 1,2-Dimethoxyethane was first refluxed over $LiAlH_4$ and distilled under nitrogen and subsequently distilled over potassium in the presence of benzophenone.

**Kinetics.** The reactions were started by mixing known prethermostated volumes of freshly prepared, nearly saturated, and filtered solutions of the complex and solutions of the amine in the thermostated cell of a Cary 17-D spectrophotometer and followed by periodically scanning the spectrum over the range 400–280 nm and/or measuring the decrease of absorbance at 320 nm as a function of time. The temperature was monitored by a precision microthermocouple, which was inserted in the reaction cell.

All kinetics were carried out in the presence of a sufficient excess of amine to ensure pseudo-first-order kinetics in the separable stages of the reaction.

## Results and Discussion

The spectrophotometric changes, in all cases, are consistent with two, well-separated, processes. The first stage is characterized by a well-defined isosbestic point at about 355 nm (the actual wavelength depending upon the entering amine) and a marked decrease in the absorbance in the range 300–350

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