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Calorimetric Study of the Oxidative Addition of Acyl Chlorides to Iridium(I) Complexes in Solution, the Standard State, and the Gas Phase

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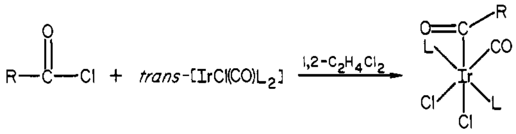
Abstract: Titration calorimetric methods have been used to determine enthalpy changes for the oxidative addition of acetyl chloride to *trans*-[IrCl(CO)L_2] (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_2(*p*-Tol), PEt_3, $P(CH_2Ph)_3$, P(*t*-Bu)Ph_2, or $P(OPh)_3$). These data were fitted to a two-parameter equation, $-\Delta H = A_0 + A_1\theta + A_2\nu$. Heats of solution and sublimation were determined for [IrCl(CO)L_2] and {$IrCl_2$[C(O)CH_3](CO)L_2} (L = PMe_3 or PEt_3). Enthalpy changes for reaction in ethylene dichloride solution, the standard state, and the gas phase were evaluated for these compounds. The enthalpies of oxidative addition of RC(O)Cl (R = Me, Et, *n*-Pr, *i*-Pr, *t*-Bu, CH_2Cl, $CHCl_2$, or Ph) to *trans*-[IrCl(CO)$(PMe_2Ph)_2$] were determined. A value of *D*(Ir–C(O)CH_3) = 205 ± 46 kJ/mol has been obtained.

We wish to report the results of our study of the thermochemistry of the acyl chloride/*trans*-[IrCl(CO)L_2] (L = tertiary phosphine) system. The oxidative addition reaction of acyl halides with d^8 metal centers and its reverse, the reductive elimination of an acyl halide or other molecules containing the acyl moiety from a d^6 metal center, are found in a wide range of important catalytic and stoichiometric reaction systems. Examples can be found in decarbonylation, acetic acid synthesis, and ketone synthesis via coupling reactions.[1-4] To date, there have been no systematic studies of the thermochemistry of this reaction type. We and others have carried out calorimetric studies of oxidative addition at square-planar d^8 centers and sought correlations of ΔH with steric and electronic effects of ligands already in the coordination sphere of the metal.[5-8] Another goal has been to derive approximations of M–R group bond energies of importance in organometallic chemistry.[6,7,9] The work reported here extends this to acid chlorides and provides a comparison of enthalpy changes for reaction in solution, in the standard state, and for the first time in the gas phase.

Results



(1)

R = CH_3 and L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_2(*p*-Tol), PEt_3, $P(CH_2Ph)_3$, P(*t*-Bu)Ph_2, or $P(OPh)_3$; L = PMe_2Ph and R = Me, Et, *n*-Pr, *i*-Pr, *t*-Bu, $ClCH_2$, Cl_2CH, or Ph

The reaction system we have studied in solution is summarized in eq 1. Many acyl complexes of the type formed in reaction 1 have been prepared and characterized by other workers[10] as well as ourselves.[11] The addition of RC(O)Cl has been found to give the isomer shown as the only product. We have isolated the reaction products and characterized them spectroscopically. The ^1H NMR and IR data are given in the Experimental Section. The Jenkins/Shaw method for bis-methyl-substituted phosphine

Table I. Heats of Reaction of *trans*-IrCl(CO)L_2 with Acetyl Chloride in 1,2-Dichloroethane at 25.00 ± 0.02 °C and Electronic and Steric Parameters of the Phosphine Ligands L

L	ΔH_{rxn},[b] kJ/mol	θ[a]	ν[a]
PMe_3	−122.2 ± 3.4	118	2064.1
PMe_2Ph	−124.3 ± 5.9	122	2065.3
$P(OPh)_3$	−70.7 ± 2.5	128	2085.3
PEt_3	−120.5 ± 6.7	132	2061.7
$PMePh_2$	−113.4 ± 4.6	136	2067.0
P(*p*-Tol)Ph_2	−105.0 ± 2.9	145	2068.2
P(*t*-Bu)Ph_2	−90.8 ± 1.7	157	2064.7
$P(CH_2Ph)_3$	−75.3 ± 4.2	165	2066.4

[a] From ref 19. [b] Error limits are one standard deviation.

Table II. Heats of Reaction of *trans*-IrCl(CO)$(PMe_2Ph)_2$ with Acyl Chlorides in 1,2-Dichloroethane at 25.00 ± 0.02 °C

acyl chloride	ΔH_{rxn},[a] kJ/mol	acyl chloride	ΔH_{rxn},[a] kJ/mol
CH_3(CO)Cl	−124.3 ± 5.9	Cl_2CH(CO)Cl	−139.8 ± 3.8
CH_3CH_2(CO)Cl	−122.6 ± 4.6	Cl_3C(CO)Cl[b]	−173.2 ± 6.3
$(CH_3)_2CH$(CO)Cl	−119.7 ± 4.2	$(CH_3)_3C$(CO)Cl[b]	−174.9 ± 8.4
$ClCH_2$(CO)Cl	−133.9 ± 3.4	C_6H_5C(O)Cl	−110.0 ± 4.1

[a] Error limits are one standard deviation. [b] Products in these two cases did not show a ν(C=O) and do not correspond to simple oxidative addition.

Scheme I

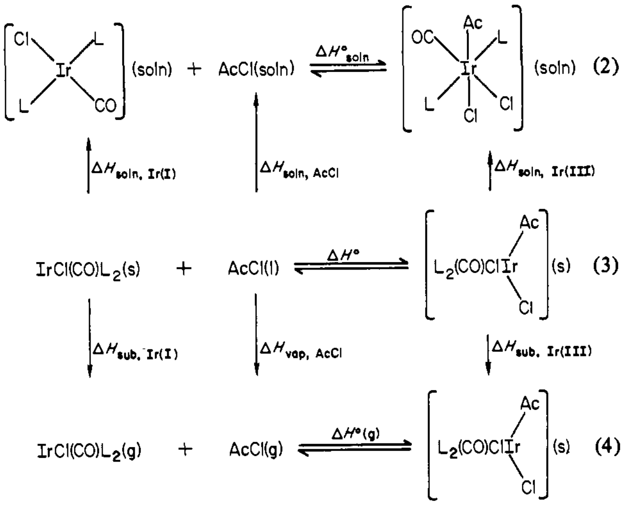


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Table III. Thermochemical Data (kJ/mol) for the Acetyl Chloride/Iridium(I) System in Solution, Standard State, and Gas Phase[a]

$IrCl(CO)L_2 + CH_3C(O)Cl \rightarrow IrCl_2(CO)[C(O)CH_3]L_2$

Δ	PMe_3	PEt_3
$\Delta H_{soln,Ir(I)}$	+16.7 ± 4.2	+19.8 ± 0.2
$\Delta H_{soln,Ir(III)}$	+16.7[b]	+17.5 ± 0.7
$\Delta H_{soln,CH_3COCl}$	+0.2 ± 0.04	+0.2 ± 0.04
$\Delta H_{sub,Ir(I)}$	+67.4 ± 15.5	+79.5 ± 9.6[c]
$\Delta H_{sub,Ir(III)}$	+67.4 ± 8.4	+71.6 ± 0.8
$\Delta H_{vap,CH_3COCl}$[d]	+30.1 ± 0.4	+30.1 ± 0.4
ΔH_{soln}	−122.2 ± 3.4	−120.5 ± 6.7
ΔH°	−121.3 ± 4.2	−118.4 ± 6.7
ΔH_{gas}	−152 ± 17	−156.1 ± 11.7

[a] Terminology refers to the reaction scheme. [b] Assumed equal to 16.7 by analogy with other compounds done, see ref 6, since its solubility was not sufficient for determination of ΔH_{soln} by using our equipment. [c] Calculated from $\Delta H_{vap} = 60.3 \pm 9.5$ kJ/mol and $\Delta H_{fus} = 19.2 \pm 0.6$ kJ/mol. [d] Reference 17.

complexes[12] and sensitivity of ν(Ir–Cl) to the ligand trans to Cl[13] allow unambiguous structural assignments. In all cases only one product was detected, within the limits of sensitivity of ^1H NMR. In those cases where the complexes have been previously characterized, our results compare favorably.

Enthalpy changes for reactions were determined by adiabatic titration calorimetry.[14] A series of aliquots of a solution of the iridium(I) complex were added to a solution containing an excess of the acyl halide (under argon). The titration curves were characteristic of reactions having a high equilibrium constant ($K > 10^4$) and in the range of concentrations studied (metal, 1–5 mM, and acyl halide, 0.1–0.5 M). ΔH was independent of the concentration of metal complex and acyl halide. Sample of the acyl halides were freshly prepared and/or distilled before use, and the values of ΔH shown in Tables I and II are the average of results for at least six determinations each for at least two independently prepared samples of iridium(I) complex. The calorimeter was calibrated by using the 0.100 N HCl/tris(hydroxymethyl)aminomethane titration. The complete thermomechanical system for solution, standard state, and gas phase reaction is shown in Scheme I. For acetyl chloride and the ligands L = trimethyl- and triethylphosphine, we have measured the heats of solution and sublimation necessary to calculate the enthalpy change for reaction in the standard state (eq 3) and in the gas phase, (eq 4). These data are given in Table III. Heats of solution for reactant and product compounds were measured as previously described.[6] The pairs of iridium complexes *trans*-$[IrCl(CO)L_2]$ and $\{IrCl_2[C(O)CH_3](CO)L_2\}$ (L = PMe_3 or PEt_3) were found to be amenable to determination of the heats of sublimation. Purification of the iridium(I) complexes by sublimation in vacuo has been reported in the literature,[15,16] and we have found that their acetyl chloride adducts, reported for the first time here, are also sublimable. The sublimed products are spectroscopically and analytically pure. IR and NMR spectroscopy establish their identity with the unsublimed substances. Mass spectra of the complexes show molecular ions for the iridium(I) complexes but the highest mass peaks for the acyliridium(III) complexes correspond to the molecular ion minus 15 mass units. Samples purified by repeated sublimation were used for the determination of their vapor pressures by using the Knudsen technique, and the heat of sublimation was evaluated from the temperature dependence of the rate of mass loss with time.[17] For *trans*-$[IrCl(CO)(PEt_3)_2]$ which melts at 78 °C in vacuo, this yielded the heat of vaporization of the liquid which was combined with the heat of fusion measured by using differential scanning calorimetry to obtain the heat of sublimation.[18] Data for the rate of mass loss and vapor pressures of these compounds are given in Table IV. The values of heats of sublimation and other thermochemical data referring to Scheme I are given in Table III.

Discussion

We have previously had success in correlating enthalpy changes for oxidative addition reactions of rhodium and iridium complexes of the Vaska type with Tolman's steric, θ, and electronic, ν, parameters[19] for tertiary phosphine ligands, using eq 5.[5] This is

$$-\Delta H = A_0 + A_1\theta + A_2\nu \quad (5)$$

of value since a correlation based on a relatively small number of compounds allows prediction of ΔH for complexes of all tertiary phosphines in Tolman's compilation. ΔH for addition of acetyl chloride to a series of complexes *trans*-$[IrCl(CO)L_2]$ was measured. Table V gives the parameters A_i determined by using data in Table I. For comparison we have tried correlations based on θ or ν alone. The eight ligands chosen for study span a wide range of cone angles, but with the exception of triphenylphosphite the range of electronic parameters is narrow. Selection of ligands was limited by the requirement that the oxidative addition reaction reach equilibrium rapidly to allow accurate determination of ΔH, using our adiabatic calorimeter.

If the data in Table I are treated with use of linear models, the following is observed. When the ΔH for the $P(OPh)_3$ complex is excluded a good fit ($R = 0.97$) is obtained by using the cone angle parameter only, model A in Table V. When the $P(OPh)_3$ value is included, the fit using the cone angle only is worsened ($R = 0.61$), model B in Table V. All of the data can also be fitted successfully to an equation linear in cone angle and electronic parameter ($R = 0.97$), model C in Table V. Equations linear in the electronic parameter alone, models D or E, give a poor fit of the data.

For investigation of the effect of the nature of the acyl halide on ΔH for oxidative addition, the complex *trans*-$[IrCl(CO)(PMe_2Ph)_2]$ was chosen as the reference complex since it reacts rapidly and cleanly with a range of acyl chlorides. The data in Table II indicate that within experimental uncertainty methyl substitution in acetyl chloride has no significant effect on ΔH and that substitution of chlorine at the α-position causes ΔH to become more exothermic. Pivaloyl chloride and trichloroacetyl chloride were found to react by a different path and did not give the simple oxidative addition product so they could not be included in the survey of compounds.

We and others have shown that enthalpy data for oxidative addition reactions can be related to metal–ligand bond enthalpies.[5-9] For calculation of these parameters, ΔH values for reaction in the gas phase are normally required. In the case of metal complexes these are usually not accessible due to low volatility and/or low thermal stability of the metal-containing compounds. This has led to the use of the assumption that the heats of sublimation of reactant and product complexes are the same and cancel from the relationship between the enthalpy for the reaction in solution, ΔH_{soln}, and that in the gas phase, ΔH_{gas} (eq 6).[20-22]

$$\Delta H(g) = \Delta H_{soln} - \Delta H_{soln,Ir(III)} + \Delta H_{soln,Ir(I)} + \Delta H_{soln,AcCl} + \Delta H_{sub,Ir(III)} - \Delta H_{sub,Ir(I)} - \Delta H_{vap,AcCl} \quad (6)$$

The other terms for heats of solution and vaporization of reactant

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Table IV. Rates of Mass Loss and Vapor Pressures of *trans*-[IrCl(CO)L_2] and {IrCl[$CH_3C(O)$](CO)L_2} (L = PMe_3 or PEt_3) as a Function of Temperature

compd	T, K	$10^6 dm/dt$, g/s	$10^4 P$, torr	cell[a]
trans-[IrCl(CO)$(PMe_3)_2$]	372.1 ± 0.5	0.155 ± 0.013	198 ± 17	1
	382.0	0.328 ± 0.023	425 ± 30	
	392.0	0.468 ± 0.001	614 ± 2	
trans-[IrCl(CO)$(PEt_3)_2$]	372.0	0.278 ± 0.003	301 ± 4[b]	1
	382.0	0.463 ± 0.012	545 ± 16[b]	
	392.0	0.708 ± 0.015	846 ± 20[b]	
{$IrCl_2$[C(O)CH_3](CO)$(PMe_3)_2$}	403.2	0.243 ± 0.008	13.9 ± 0.5	2
	413.6	0.451 ± 0.080	26.3 ± 4.1	
	424.7	0.707 ± 0.012	41.7 ± 0.7	
$IrCl_2$[C(O)CH_3](CO)$(PEt_3)_2$	371.0	(4.03 ± 0.60) × 10^{-2}	2.06 ± 0.31	2
	381.0	(6.75 ± 0.38) × 10^{-2}	3.50 ± 0.20	
	388.0	(11.27 ± 0.17) × 10^{-2}	5.93 ± 0.09	

[a] For cells no. 1 and no. 2 the area of the openings are (1.28 ± 0.1) × 10^{-4} and (2.72 ± 0.10) × 10^{-3} cm^2. [b] For the liquid.

Table V. Models Used to Fit ΔH Data from Table I for Reaction of CH_3COCl with *trans*-[IrCl(CO)L_2] to a Linear Equation of the Type $-\Delta H = A_0 + A_1\theta + A_2\nu$[a]

model		A_0	A_1	A_2	R[b]
A	without $P(OPh)_3$ let $A_2 = 0$	+253.4	−1.046	0	0.97
B	with $P(OPh)_3$ let $A_2 = 0$	+212.9	−0.7970	0	0.61
C	with $P(OPh)_3$	+4881.2	−0.9325	−2.248	0.97
D	with $P(OPh)_3$ let $A_1 = 0$	+4153.9	0	−1.959	0.66
E	without $P(OPh)_3$ let $A_1 = 0$	+6930.3	0	−3.303	0.38

[a] θ = cone angle; ν = electronic parameter. From ref 19. [b] R = correlation coefficients.

and product complexes and organic substrate are normally known or experimentally accessible. Usually the assumption concerning heat of sublimation has been used when no test of its validity was possible.

We have determined heats of sublimation and other parameters for two sets of iridium complexes so that ΔH_{soln}, $\Delta H°$, and ΔH_{gas} can be compared. The data are summarized in Table III. The heats of sublimation of iridium(I) and corresponding iridium(III) complexes are in fact the same within the limits of experimental uncertainty for the two pairs of compounds we have studied. Because the heats of solution of reactant and product complexes are usually close in value,[6] ΔH for reaction in solution is, within experimental error, the same as $\Delta H°$ for the standard state. The gas-phase enthalpy change for the cases reported here differs significantly from these only because of the contribution due to the heat of vaporization of acetyl chloride. This then indicates that for closely related pairs of compounds the assumption of comparable heats of sublimation is a reasonable one. It is justified since in many cases the resulting approximate bond energies are the only data available and more accurate values are not likely to be available soon for highly substituted complexes.

The gas-phase enthalpy change is related to the dissociation energies of the bonds broken and formed during the reaction by eq 7. The terms for iridium compounds refers to dissociation

$$\Delta H(g) = D(CH_3C(O)\text{–}Cl) - D(Ir\text{–}C(O)CH_3) - D_{II}(Ir\text{–}Cl) \tag{7}$$

energies of $Cl_2L_2(CO)Ir\text{–}C(O)CH_3$ and $ClL_2(CO)Ir\text{–}Cl$, respectively. A value of D(Ac-Cl) can be calculated from available heats of formation of acetyl chloride,[17] chlorine atom,[23] and acetyl radical[24] and is 349 ± 4 kJ/mol. Combination of this value with $\Delta H(g)$ from Table III gives a value of 501 ± 18 kJ/mol for the sum of the Ir–Cl and Ir–C(O)CH_3 bond energies (L = PMe_3). An approximate value of the mean Ir–Cl bond energy has been derived from heats of the oxidative addition of dichlorine to Vaska's complex, $\bar{D}(Ir\text{–}Cl) \approx 297 \pm 42$ kJ/mol.[5] Combination of this with the above data gives $D(Ir\text{–}C(O)CH_3) = 205 \pm 46$ kJ/mol. In previous work on reactions of organic iodides or diiodine with *trans*-[IrCl(CO)$(PMe_3)_2$] we have determined an approximate $D(Ir\text{–}C(O)CH_3) = 188 \pm 12$ kJ/mol, on the basis of the data in the solution phase.[6,7] This is comparable to the value of D(Pt–C(O)Ph) = 180 kJ/mol for *trans*-{PtCl[PhC(O)]$(PPh_3)_2$} which has been reported by Ashcroft and co-workers.[25] Although the uncertainties in these values are large, they are indicative of the magnitude of the metal–acyl bond strength.

Experimental Section

The complexes *trans*-[IrCl(CO)L_2] (where L = PMe_3,[15] PMe_2Ph,[5] $PMePh_2$,[26] $PPh_2(p\text{-Tol})$, $P(CH_2Ph)_3$, $P(OPh)_3$, and $P(t\text{-Bu})Ph_2$[27]) were prepared by methods in the literature. These were stored in sealed ampules, each of which contained enough sample for one experiment. Phosphines were prepared by the Grignard method or purchased from Strem Chemical Co. Acetyl chloride, isobutyryl chloride, *n*-butyryl chloride, and pyvalyl chloride were commercial samples and were freshly distilled before use. Propionyl chloride and mono-, di- and trichloroacetyl chloride were prepared by methods in the literature.[28] 1,2-Dichloroethane was distilled from P_4O_{10} prior to use. Mass spectra were obtained by using a Du Pont 321 spectrometer via the direct sample inlet. All the melting points were determined on a Mel-Temp apparatus. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer and ^1H NMR spectra were obtained using a Varian T-60 spectrometer. A Perkin-Elmer DSC-1B was used to determine heats of fusion. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

***trans*-[IrCl(CO)$(PMe_3)_2$].** The complex was prepared by the method in the literature,[15] and samples were purified by at least three sublimations at 100 °C: mp 176–181 °C (in vacuo); IR (Nujol) 1940 (IrC≡O) cm^{-1}; mass spectrum, *m/z* (relative intensity) 410 (11.1), 408 (47.3), 406 (23.6), 382 (27.3), 380 (100), 378 (49.7), 344 (69.6), 342 (43.5), 329 (12.4), 328 (18.6), 327 (11.1), 326 (22.4), 314 (13.6), 313 (47.3), 312 (22.4), 311 (33.5), 310 (13.6), 301 (11.1), 300 (61.0), 299 (17.4), 298 (44.8), 297 (17.3), 295 (12.4), 283 (17.4), 281 (17.4), 269 (13.6), 268 (13.6), 267 (12.4).

Chlorocarbonylbis(triethylphosphine)iridium. Hydridodichlorocarbonylbis(triethylphosphine)iridium(III), ($IrHCl_2(CO)(PEt_3)_2$) was prepared in the following way. Concentrated hydrochloric acid (7.5 mL) and 37.5 mL of 2-methoxyethanol were added to 3.2 g of iridium trichloride hydrate, and the mixture was stirred under nitrogen for 2 h at room temperature. Carbon monoxide was then bubbled through the solution which was vigorously stirred at reflux overnight. The system was open to allow further loss of hydrogen chloride. The color of the solution turned from brownish red to red to greenish yellow. The solution was cooled to room temperature, and 3.3 mL triethylphosphine (67% in isopropanol) was added. The product separated as white prisms upon cooling of the solution in an ice bath. The yield is 2.98 g (62%): mp 93–95 °C; IR (Nujol) 2188 (IrH), 2012 (IrC≡O), 308 (IrCl, trans to CO), 261 (IrCl, trans to H) cm^{-1}.

trans-IrCl(CO)$(PEt_3)_2$ was prepared as follows. The iridium(III) hydride ($IrHCl_2(CO)(PEt_3)_2$, 2.98 g) in 10 mL of methanol was treated with 7.5 mL of 1.1 M sodium methylate, and the mixture was refluxed

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gently for a few minutes under nitrogen. The clear solution was transferred under N_2 to a low-temperature filter cooled in a dry ice–acetone bath. After the completion of transfer, the mixture was cooled for about 40 min and then filtered. The solid was washed with cold methanol–ether (1:1). The product is yellow prisms which were dried in vacuo. The yield is 2.44 g (88%). The crude product distills onto a cold finger at 100 °C (1–2mm Hg). After purification the yield is 2.17 g (78%): mp 78–80 °C (n vacuo); IR (Nujol) 1929 ($IrC\equiv O$), 309 (IrCl) cm^{-1}; mass spectrum *m/z* (relative intensity) 494 (70), 492 (40), 490, 466 (40), 464 (60), 462 (40), 437 (50), 436 (30), 435 (50), 408 (70), 406 (90, 404 (40), 381 (50), 379 (60), 377 (30), 371 (40), 369 (50), 368 (50), 367 (30), 366 (60), 364 (40), 343 (50), 342 (30), 341 (60), 340 (70), 339 (60), 338 (60), 337 (30), 336 (60), 335 (30), 334 (50), 310 (50), 308 (40), 119 (80), 118 (50), 117 (100).

Preparation of {$IrCl_2(CO)[CH_3C(O)](PMe_3)_2$}. *trans*-[$IrCl(CO)(PMe_3)_2$] (0.1 g) was placed in a 25-mL round-bottom flask. The flask was purged with N_2 for 15–20 min. Then 1 mL of 1,2-dichloroethane and 4–5 drops of acetyl chloride which were purged with N_2 were added. The resulting yellow solution was stirred until it turned colorless (~5–10 min). Next 10 mL of hexane was added, and the resulting mixture was allowed to stand in an ice bath for 0.5 h. The crude product was isolated by filtration, washed with 5 mL of cold hexane, and dried in vacuo. The product was recrystallized from 1,2-dichloroethane and hexane. The compound can also be purified by sublimation at 100 °C, in vacuo: percent yield 70–75% (0.085–0.090 g); cream-colored solid; mp 216–218 °C (in vacuo); IR (Nujol) 2036 ($IrC\equiv O$), 1627 ($C{=}O$), 302 (IrCl) cm^{-1}; NMR ($CDCl_3$) δ 1.82 (t, PCH_3), 2.32 (s, CH_3); mass spectrum, *m/z* (relative intensity) 473 (20), 471 (30), 469 (20), 458 (20), 445 (20), 443 (30), 441 (20), 417 (40), 415 (70), 413 (20), 113 (30), 111 (100), 77 (30), 76 (50), 75 (70), 61 (30), 59 (20).

Anal. Calcd for {$IrCl_2[C(O)CH_3](CO)[P(CH_3)_3]_2$}: C, 22.21; H, 4.31. Found: C, 22.21; H, 4.36.

{$IrCl_2[CH_3C(O)](CO)(PEt_3)_2$}. This was prepared in a manner similar to that of the previous complex starting with 0.1 g of [$IrClCO(PEt_3)_2$] and using toluene instead of 1,2-dichloroethane as solvent. This complex can be sublimed onto a cold finger (25 °C) at 100 °C in vacuo: percent yield 75–80%; cream-colored solid, mp 116–118 °C (in vacuo); IR (Nujol) 2028 ($IrC\equiv O$), 1618 ($C{=}O$), 317 (IrCl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19 (m, PCH_2CH_3), 2.21 (m, PCH_2CH_3), 2.38 (s, $C(O)CH_3$); mass spectrum, *m/z* (relative intensity) 531 (14), 529 (29), 527 (12), 502 (23), 500 (47), 498 (19), 496 (11), 494 (36), 493 (16), 492 (19), 466 (14), 465 (11), 464 (22), 463 (11), 463 (16), 368 (12), 366 (18), 364 (11), 346 (14), 344 (18), 343 (11), 342 (16), 341 (14), 340 (20), 339 (14), 338 (23), 337 (11), 336 (21), 334 (19), 318 (12), 317 (10), 316 (13), 315 (13), 314 (12), 313 (12), 312 (19), 311 (17), 310 (40), 308 (38), 306 (20), 282 (21), 280 (27), 278 (22), 155 (7), 153 (18), 118 (6), 117 (11), 89 (100), 75 (47).

Anal. Calcd for {$IrCl_2[C(O)CH_3](CO)[P(C_2H_5)_3]_2$}: C, 31.57; H, 5.79. Found: C, 31.50; H, 5.82.

***trans*-{$IrCl_2[C(O)R](CO)L_2$}.** Excess acyl chloride, ca. 0.2 mL, was added to a solution of 0.1 g of *trans*-[$IrCl(CO)L_2$] in 5 mL of ethylenedichloride under a flow of N_2. After the excess acyl chloride and 1,2-dichloridoethane were evaporated off, methanol was added to the oily residue. The crystalline product was collected by filtration in air. These were characterized spectroscopically. (R = CH_3 and L = PMe_2Ph:[10] IR (Nujol) 2063, 2040 ($C\equiv O$), 1623 ($CH_3C{=}O$), 310, 234 (IrCl) cm^{-1}; NMR ($CDCl_3$, 1% Me_4Si) δ 2.07 (t), 2.13 (t, PCH_3), 1.45 (s, $CH_3C(O)$). L = $PMePh_2$:[11] IR (Nujol) 2058 ($C\equiv O$), 1625 ($C{=}O$), 309, 240 (IrCl) cm^{-1}; NMR ($CDCl_3$) δ 2.50 (t, PCH_3), 0.65 (s, CH_3CO). L = PPh_2-(*p*-Tol): IR (Nujol) 2057 ($C\equiv O$), 1612 ($C{=}O$), 301, 220 (IrCl) cm^{-1}; NMR ($CDCl_3$) δ 2.31 (s, $CH_3C(O)$), 3.67 (s, $C_6H_5CH_3$). L = $P(CH_2Ph)_3$: IR (Nujol) 2050 ($C\equiv O$), 1639 ($C{=}O$), 303, 225 (IrCl) cm^{-1}; NMR ($CDCl_3$) δ 2.13 (s, $CH_3C(O)$), δ 3.57, 3.62, 3.67 (three triplets, $P(CH_2C_6H_5)_3$).

L = PPh_2(*t*-Bu): IR (Nujol) 2062, 2041 ($C\equiv O$), 1682 ($C{=}O$), 305, 255 (IrCl) cm^{-1}. L = $P(OPh)_3$: IR (Nujol) 2077 ($C\equiv O$), 1644 ($C{=}O$), 303, 252 (IrCl) cm^{-1}; NMR ($CDCl_3$) δ 2.49 (s, CH_3CO).

L = PMe_2Ph and R = C_2H_5:[10] IR (Nujol) 2046, 2030 ($C\equiv O$), 1637 ($C_2H_5C{=}O$), 305, 236 (IrCl) cm^{-1}; NMR ($CDCl_3$, 1% Me_4Si) δ 2.06 (t), 2.16 (t, PCH_3), 0.13 (t, J = 7.0 Hz, CH_3CH_2CO), 1.83 (q, J = 8.0 Hz, CH_3CH_2CO). R = $(CH_3)_2CH$: IR (Nujol) 2031 ($C\equiv O$), 1671 ($C_3H_7C{=}O$), 308, 233 (IrCl) cm^{-1}; NMR ($CDCl_3$) δ 2.00 (t), 2.16 (t, PCH_3), 0.35 (d, J = 7 Hz, $(CH_3)_2CH$), 1.25 (m, $(CH_3)_2CH$). R = CH_2Cl: IR (Nujol) 2055, 2042 ($C\equiv O$), 1646 ($C{=}O$), 306, 246 (IrCl) cm^{-1}; NMR ($CDCl_3$) δ 2.04 (t), 2.12 (t, PCH_3), 3.40 (s, CH_2Cl). R = $CHCl_2$: IR (Nujol) 2053 ($C\equiv O$), 1693 ($C{=}O$), 303, 233 (IrCl) cm^{-1}; NMR ($CDCl_3$) δ 2.05 (t), 2.17 (t, PCH_3), 5.77 (s, $CHCl_2$). $R = C_6H_5$:[10] IR (Nujol) 2057, 2038 ($C\equiv O$), 1643 ($C{=}O$), 294, 246 (IrCl) cm^{-1}; NMR ($CDCl_3$) δ 1.93 (t), 2.5 (t, PCH_3).

Calorimetry. The procedure and Tronac 450-4 calorimeter system has been previously described as has the method for determining heats of solution of reactants and products. In general 0.02–0.04 g of the iridium(I) complex was placed in a 2-mL volumetric flask. The flask was purged with N_2 for 25–30 min, and then 1,2-dichloroethane, purged with N_2, was added to the mark and the solution (titrant) transferred to the titration buret under a slow stream of N_2. The acyl halide was degassed with N_2 for 20–30 min and a known amount added (0.5–1.5 mL) via syringe through the Teflon delivery line to the reaction Dewar, which had been previously purged with argon for 25–30 min. Enough 1,2-dichloroethane was added via syringe through the Teflon delivery line to give total volume of 40 mL. Aliquots of the metal solution were added, and the reaction heat, Q, was determined. The titration curves are characteristic of reactions having large equilibrium constants ($K > 10^4$), and Q was independent of iridium(I) or acyl halide concentration in the range studied. The calorimeter was calibrated by using the 0.100 M HCl/tris(hydroxymethyl)aminomethane titration, $\Delta H = -47.49 \pm 0.96$ kJ/mol (lit.[14] −47.49).

Measurement of Vapor Pressures and Heats Of Sublimation of Iridium Complexes. The Knudsen effusion technique was used to determine vapor pressures.[17] The Knudsen cell was constructed from a 0.25-in. stainless-steel Swagelok cap with a circle of stainless-steel sheet having a small hole drilled in it silver soldered over the opening. The cell was placed in a Pyrex container constructed from a drying pistol which was attached to a constant dynamic vacuum of ca. 10^{-5} torr. The jacket surrounding the Knudsen cell was heated by refluxing solvent. Temperature stability over the period of days was ±0.5 K. Weight losses were measured as a function of time by periodically removing the cell and weighting it and its contents on a Mettler microanalytical balance. The area of the opening in the Knudsen cell, a, was determined by calibration with benzoic acid. The vapor pressure of the complexes was then determined by using the equation

$$P = \frac{\mathrm{d}m/\mathrm{d}t}{a}(2\pi RT/M)^{1/2}$$

where $\mathrm{d}m/\mathrm{d}t$ is the rate of mass loss in g/s, T is the absolute temperature, and m is the molecular weight of the vapor. The values of $\mathrm{d}m/\mathrm{d}t$ were determined by least-squares techniques at three temperatures. Since $\mathrm{d}m/\mathrm{d}t$ is proportional to the vapor pressure, plots of $\ln(\mathrm{d}m/\mathrm{d}t)$ vs. $1/T$ were used to calculate the heats of vaporization. Correlation coefficients were 0.96 or better for all plots of mass loss with time or $\ln(\mathrm{d}m/\mathrm{d}t)$ vs. $1/T$. Data are given in Tables III and IV. In the temperature range studied *trans*-[$IrCl(CO)(PEt_3)_2$] was a liquid so ΔH_{vap} was determined. The heat of fusion of this compound was measured under an N_2 atmosphere by differential scanning calorimetry.

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