brated under the reaction conditions with partial consumption of **5c** (see last line of Table I). This is the likely reason that reaction of Me$_2$N· with 6/94 (thermodynamically equilibrated) cis/trans **5a** gives a poor correspondence between isomeric ratios of reacted **5a** and product **5c** as well as a poor yield of **5c**. The dominant *trans*-**5a** is less reactive than is *cis*-**5a**, hence dimethylamino radicals react rapidly with *cis*-**5c** leading finally to its equilibration with *trans*-**5c**. Note, however, that the trans/cis ratio for product **5c** from reaction of 6/94 **5a** is reduced as expected for an inversion pathway.

When **5b** is the reactant, the minor trans-isomer is the thermodynamically less stable form[8] and the more reactive isomer toward Me$_2$N·. The data again argue for *inversion about phosphorus as the predominant pathway*. Yields of PhCH$_2$CH$_2$Ph as high as 80% attest to the free-radical nature of the displacement on **5b**.

We interpret these results (inversion) to mean that if a phosphoranyl radical is involved in these processes, its geometry must be such that X and Y are either coaxial or coequatorial. The attacking radical Me$_2$N· clearly is not introduced into the phosphoranyl intermediate in a configurationally random manner, a result consistent with earlier conclusions drawn from investigations of reactions of alkoxy radicals with trialkyl phosphites.[2] If as assumed above, X· enters the intermediate axially, and the odd electron *is equatorial*, then *structure 4 will give the observed stereochemistry*.

Since the alkyl substituents on phosphorus are relatively electropositive and according to esr results[3] appear to exhibit an equatorial preference in the most thermodynamically stable form of intermediates such as Me$_3$PO-*t*-Bu and Me$_2$P(OR)$_2$, kinetic factors may favor formation of **4**. Alternatively, the stereochemistry of these systems may be controlled by the presence of the six-membered ring which in pentacovalent systems has been suggested[11] to have a thermodynamic preference for diequatorial attachment to phosphorus. Finally, the particular systems investigated may react *via* a concerted (synchronous S$_H$2) mechanism. These possibilities are being investigated.

(11) P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **10**, 687 (1971).

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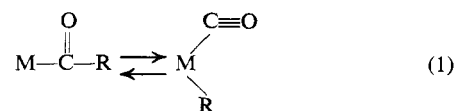Salt Lake City, Utah 84112*

Direct Determination of the Enthalpy Change for the Migration of Para-Substituted Benzyl and Trifluoromethyl Groups in Coordinatively Unsaturated Iridium(III) Acyl Complexes
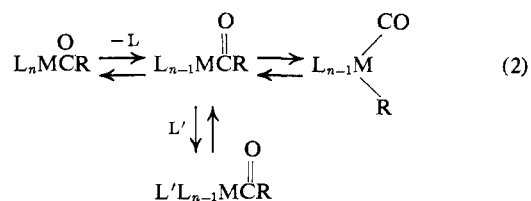
Sir:

The insertion of carbon monoxide into a metal–carbon bond or its reverse, the migration of an alkyl or aryl group from an acyl carbon to a metal site in an acyl complex, are of widespread occurrence in organo-

metallic syntheses and homogeneous catalytic processes.[1] A reaction sequence which accounts for what is known of the mechanism for these transformations is shown in
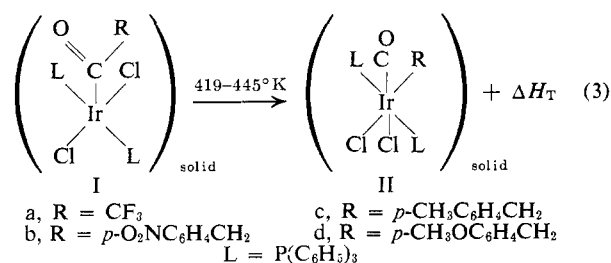
$$M-\overset{\overset{\text{O}}{\|}}{C}-R \; \underset{\longleftarrow}{\overset{\longrightarrow}{}} \; M\overset{\text{C}\equiv\text{O}}{\underset{\text{R}}{\diagup}} \qquad (1)$$

eq 2.[1] In general the intermediate of reduced coordi-

$$L_nM\overset{\overset{\text{O}}{\|}}{C}R \; \underset{\longleftarrow}{\overset{-\text{L}}{\rightleftharpoons}} \; L_{n-1}M\overset{\overset{\text{O}}{\|}}{C}R \; \underset{\longleftarrow}{\overset{\longrightarrow}{}} \; L_{n-1}M\overset{\text{CO}}{\underset{\text{R}}{\diagup}} \qquad (2)$$

$$L' \underset{\text{L}'L_{n-1}M\overset{\overset{\text{O}}{\|}}{C}R}{\overset{\uparrow\downarrow}{}}$$

nation number, L$_{n-1}$MC(O)R, is not detected and the actual migration (or insertion) step is not observed independent of the loss (or addition) of a ligand from the metal coordination sphere. It is not surprising, then, that no thermochemical data have yet been reported for the reaction step in which the alkyl or aryl group migrates to or from the coordinated CO group.

In 1971 Kubota, Blake, and Smith reported the synthesis of a series of five-coordinated phenylacetyl complexes of iridium(III).[2a] These compounds were used as models for the coordinatively unsaturated intermediate in eq 2, and the rate of the migration step was studied.[2] We now wish to report that these five-coordinated phenylacetyl complexes, as well as the analogous trifluoroacetyl complex,[2b] undergo the migration reaction in the solid state. This has made it possible to determine the enthalpy change, ΔH_T, at the reaction temperature, T, and at standard conditions, ΔH_0.

The reaction studied is shown in eq 3. When the

$$\left(\begin{array}{c} \text{O} \quad \text{R} \\ \diagdown \diagup \\ \text{L} \quad \text{C} \quad \text{Cl} \\ \diagdown \quad | \quad \diagup \\ \text{Ir} \\ \diagup \quad \diagdown \\ \text{Cl} \qquad \text{L} \end{array}\right)_{\text{solid}} \xrightarrow{419-445°\text{K}} \left(\begin{array}{c} \text{O} \\ \text{L} \quad \overset{\|}{\text{C}} \quad \text{R} \\ \diagdown \; | \; \diagup \\ \text{Ir} \\ \diagup | \diagdown \\ \text{Cl} \; \text{Cl} \; \text{L} \end{array}\right)_{\text{solid}} + \Delta H_T \quad (3)$$

I	**II**
a, R = CF$_3$	c, R = *p*-CH$_3$C$_6$H$_4$CH$_2$
b, R = *p*-O$_2$NC$_6$H$_4$CH$_2$	d, R = *p*-CH$_3$OC$_6$H$_4$CH$_2$

L = P(C$_6$H$_5$)$_3$

orange solid, Ia–d, is heated to a temperature, T, which depends on the R group, the migration reaction occurs to give white compounds IIa–d. These were shown to be identical with the products formed in homogeneous solution by ir spectroscopy. The reaction was not complicated by weight loss and the exothermic peak for the migration reaction was well separated from the melting transition of the product. The enthalpy change for the reaction was determined at temperature T by standard differential calorimetric methods.[3,4] These

(1) A. Wojcicki, *Advan. Organometal. Chem.*, **11**, 87 (1973).
(2) (a) M. Kubota, D. M. Blake, and S. A. Smith, *Inorg. Chem.*, **10**, 1430 (1971); (b) D. M. Blake, S. Shields, and L. Wyman, *ibid.*, **13**, 1595 (1974).
(3) A Perkin-Elmer Model DSC-1B differential scanning calorimeter was used in the study. Peak areas for the reaction were calibrated with respect to the heat of fusion of standard indium samples. A sapphire sample was used as a standard for the heat capacity determinations.
(4) (a) W. J. Smothers and Y. Chiang, "Handbook of Differential Thermal Analysis," Chemical Publishing Co., New York, 1966; (b) Instructions for Differential Scanning Calorimetry, Perkin-Elmer Corporation Publication No. 990-9556 (1966); (c) M. J. O'Neill, *Anal. Chem.*, **38**, 1331 (1966).

Table I. Thermodynamic and Kinetic Parameters for an Alkyl Group Migration in Iridium(III) Complexes

$$\{IrCl_2[C(O)R][P(C_6H_5)_3]_2\}_{solid} \longrightarrow \{IrCl_2(CO)(R)[P(C_6H_5)_3]_2\}_{solid}$$

R	$T,^a$ °K	$\Delta H_T,^b$ kJ mol^{-1}	Standard deviation of ΔH_T (kJ mol^{-1})	$\int_{298}^{T}\Delta C_p dT$ (kJ mol^{-1})	$\Delta H_0,$ kJ mol^{-1}	$t_{1/2}$ (in solution) (min)	$\Delta H^{\ddagger}$ (in solution) (kJ mol^{-1})
Ia, CF$_3$	445	−83.88	3.8	0.08	−84 ± 4	44.59^d (at 343 °K)	+86.5
Ib, p-NO$_2$C$_6$H$_4$CH$_2$−	444	−16.40	1.30	0.01	−16 ± 1	29.67^{d,e} (at 303 °K)	+84.5^d
Ic, p-CH$_3$C$_6$H$_4$CH$_2$−	428	−14.39	1.51		−14 ± 2^c	13.83^{d,e} (at 303 °K)	+68.2^d
Id, p-CH$_3$OC$_6$H$_4$CH$_2$−	419	−13.34	3.81		−13 ± 4^c	12.57^{d,e} (at 303 °K)	+62.8^d

^{a} Temperature of peak maximum. ^{b} Each value is the average of 12 determinations. ^{c} $\Delta H_0 = \Delta H_T$ by analogy with compounds Ia and Ib. ^{d} Ia in toluene, Ib, c, and d, in benzene. ^{e} M. Kubota, D. Blake, and S. Smith, *Inorg. Chem.*, **10**, 1430 (1971).

Table II. Heat Capacity Data, $C_p = (a + bT + cT^2 + dT^3)$ (4.184 J °K^{-1} mol^{-1})

| Compound^a	a	b	c	d	$\int_{298}^{T}C_p dT$ (kJ mol^{-1})	T^b
IrCl$_2$[C(O)CF$_3$]L$_2$	179.49	1.8279 × 10^{-1}	−2.0533 × 10^{-3}	4.83 × 10^{-6}	131.67	445 °K
IrCl$_2$(CO)CF$_3$L$_2$	128.26	−1.2987	7.5246 × 10^{-3}	9.02 × 10^{-6}	131.75	
IrCl$_2$[C(O)CH$_2$C$_6$H$_4$NO$_2$]L$_2$	−39.686	1.3955	−2.8362 × 10^{-3}	3.01 × 10^{-6}	145.81	444 °K
IrCl$_2$(CO)(CH$_2$C$_6$H$_4$NO$_2$)L$_2$	−71.013	2.4474	−779.67 × 10^{-3}	9.29 × 10^{-6}	145.82	

^{a} L = P(C$_6$H$_4$)$_3$. ^{b} T = temperature at which the migration reaction occurs.

data are shown in Table I. In order to determine the enthalpy change at standard conditions, ΔH_0, the following relation was used

$$\Delta H_0 = \Delta H_T - \int_{298}^{T} \Delta C_p dT$$

Molar heat capacities, C_p, were determined for the pairs of compounds Ia and IIa and Ib and IIb using differential scanning calorimetry.[4c] The data for C_p as a function of temperature were fitted to a third degree polynomial equation in T from 298° to the reaction temperature for each compound. The integrals were then evaluated using Simpson's rule.[5] These data are shown in Table II. The magnitude of the integral term for ΔC_p was much smaller than the standard deviation in ΔH_T so that ΔH_0 may be assumed to be equal to ΔH_T. These data are shown in Table I, along with kinetic data for the reaction in homogeneous solution.

The magnitude of the enthalpy change is smaller than metal–carbon monoxide bond energies (*ca.* 120–170 kJ mol^{-1})[6] or metal–carbon bond energies (*ca.* 150–300 kJ mol^{-1}).[7] The enthalpy change is opposite in sign from that found for the decarbonylation of benzoyl platinum complexes (eq 4) for which $\Delta H = +18.6$ to

$$[P(C_6H_5)_4]_2PtCl[C(O)C_6H_4X] \longrightarrow$$
$$[P(C_6H_5)_3]_2PtCl(C_6H_4X) + CO \quad (4)$$
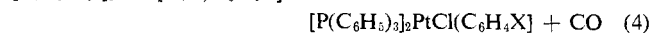
$+33.9$ kJ mol^{-1} depending on the substituents on the phenyl group.[8] In this reaction the carbon monoxide does not remain coordinated to the metal.

From the data it can be noted that there is an inverse correlation between the migration rate and the enthalpy change. The enthalpy change in solution is anticipated to be close in value to that in the solid state since heats of solution of the compounds I and II are likely to be small and of similar magnitude in nonpolar solvents. The large difference in the magnitude of ΔH_0 for the tri-

fluoromethyl, -83 kJ mol^{-1}, and benzyl groups, *ca.* -15 kJ mol^{-1}, is noteworthy. The enthalpy change for the migration reaction includes four bond energy terms (Ir—C≡O, Ir—C(O)R, Ir—R, and C(O)—R). Unfortunately there is not at present sufficient information available about the individual contributions to make a meaningful discussion of the difference in the overall values of ΔH possible. A kinetic and calorimetric study is now in progress for the series of five-coordinated complexes analogous to I where R = CF$_n$H$_{3-n}$ ($n = 3, 2, 1,$ or 0). Preliminary results show that the enthalpy change for reaction 3 decreases in the series CF$_3$ > CF$_2$H > CFH$_2$ > CH$_3$ ≈ p-XC$_6$H$_4$CH$_2$. Other work is in progress to extend the data to other migrating groups and to seek correlations of the enthalpy changes with kinetic and spectral parameters of the complexes.

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(7) G. Wilkinson, *Pure Appl. Chem.*, **30**, 627 (1972).
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MINDO/3 Study of the Bisdehydrobenzenes

Sir:

While the three bisdehydrobenzenes **1, 2,** and **3** were characterized some years ago by Berry, *et al.*,[1–3] while the ortho isomer **1** (benzyne) has been proposed as an

(1) R. S. Berry, G. N. Spokes, and M. Stiles, *J. Amer. Chem. Soc.*, **84**, 3570 (1962).
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