Evidence for an Anionic Intermediate in the Mechanistic Pathway of the Oxidative Addition Reaction of [(cyclo-octadiene)IrCl(PEtPh$_2$)] with Hydrochloric Acid

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Summary [(cod)IrCl(PEtPh$_2$)] reacts with HCl to form the oxidative addition product [(cod)IrHCl$_2$(PEtPh$_2$)] *via* the intermediate [(cod)IrCl$_2$(PEtPh$_2$)]$^-$ (cod = cyclo-octadiene).

IT has generally been found that in oxidative addition reactions of organometallic complexes the oxidation of the substrate precedes the nucleophilic attack of the anionic species of the addenda molecule.[1] We have studied the oxidative addition reaction (1) kinetically and have found

$$[\text{(cod)IrCl(PEtPh}_2)] + \text{HCl} \xrightarrow[25\ ^\circ\text{C}]{\text{MeOH}} [\text{(cod)IrHCl}_2(\text{PEtPh}_2)] \quad (1)$$

the first example of the oxidizing step being preceded by the nucleophilic attack to form the intermediate [(cod)IrCl$_2$(PEtPh$_2$)]$^-$ (cod = cyclo-octadiene).

The kinetic runs were measured on a Durrum stopped-flow apparatus by following the disappearance of [(cod)IrCl(PEtPh$_2$) ($\epsilon_{442} = 907$) under pseudo first-order conditions in dioxygen-free methanol solutions with constant ionic strength. Conductivity measurements showed HCl to be extensively dissociated (the methanol solutions contained *ca.* 2% water) thus $[\text{H}^+] = [\text{Cl}^-] =$ *ca.* $[\text{HCl}]_0$ ($[\text{HCl}]_0$ = hydrochloric acid concentration if dissociation is disregarded). The empirical rate law found for reaction (1) is shown in equation (2) where C_1 and C_2 are constants.

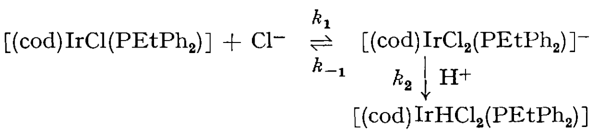
$$[\text{HCl}]_0/k_{\text{obs}} = (1/C_1) + (C_2/[\text{HCl}]_0) \quad (2)$$

The empirical rate law found when [H$^+$] was varied independently by addition of HClO$_4$ to a HCl solution is shown in equation (3) where C_3 and C_4 are constants.

$$1/k_{\text{obs}} = C_3 + (C_4/[\text{H}^+]) \quad (3)$$

These data cannot be explained by HCl reacting as a molecule or as radical species. (No change in reaction rate was found with addition of a radical trap, hydroquinone, to the reaction solutions.) The rate law shown in equation (4) can be derived from the reaction shown in Scheme 1

$$k_{\text{obs}} = (k_1k_2[\text{H}^+][\text{Cl}^-])/(k_{-1} + k_2[\text{H}^+]) \quad (4)$$

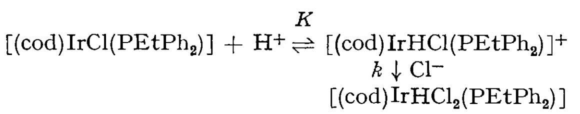


$$\begin{tikzcd}[\text{(cod)IrCl(PEtPh}_2)] + \text{Cl}^- \arrow[r, shift left, "k_1"] & {[\text{(cod)IrCl}_2(\text{PEtPh}_2)]^-} \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_2\ \text{H}^+"] \\ & {[\text{(cod)IrHCl}_2(\text{PEtPh}_2)]}\end{tikzcd}$$

SCHEME 1

{assuming [(cod)IrCl$_2$(PEtPh$_2$)]$^-$ to be in a steady state} which fits both empirical rate laws in equations (2) and (3). The k_2K_1 value calculated from the data obtained from the empirical rate law in equation (2) is 4.8×10^2 s^{-1} l^2 mol^{-2} and the value calculated from that from the rate law in equation (3) is $5{\cdot}3 \times 10^2$ s^{-1} l^2 mol^{-2}, while k_1 is *ca.* $2{\cdot}5 \times 10^2$ s^{-1} l mol^{-1}.

It is also possible to explain the empirical rate laws in equations (2) and (3) with a mechanism whereby the protonation step precedes the nucleophilic attack (Scheme 2) since



$$\begin{tikzcd}[\text{(cod)IrCl(PEtPh}_2)] + \text{H}^+ \arrow[r, leftrightharpoons, "K"] & {[\text{(cod)IrHCl(PEtPh}_2)]^+} \arrow[d, "k\ \text{Cl}^-"] \\ & {[\text{(cod)IrHCl}_2(\text{PEtPh}_2)]}\end{tikzcd}$$

SCHEME 2

the rate law derived from this reaction scheme is as shown in equation (5).

$$k_{\text{obs}} = kK[\text{H}^+]\,[\text{Cl}^-]/(1 + K[\text{H}^+]) \quad (5)$$

This implies that in order for the [H^+] dependence to limit, the equilibrium K will have to lie far over to the r.h.s. at high [H^+]. This is, however, not so since $HClO_4$ does not react with [(cod)IrCl($PEtPh_2$)] and the intermediate [(cod)IrCl_2($PEtPh_2$)]$^-$ is left to account for all the observed data.

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[1] J. K. Stille and K. S. Y. Lau, *J. Amer. Chem. Soc.*, 1976, **98**, 5841 and references therein; U. Belluco, M. Guistiniani, and M. Graziani, *ibid.*, 1967, **89**, 6494; U. Belluco, U. Croatto, P. Uguagliati, and R. Pietropaolo, *Inorg. Chem.*, 1967, **6**, 718; R. Romeo, D. Minniti, S. Lanza, P. Uguagliati, and U. Belluco, *Inorg. Chim. Acta.*, 1976, **19**, L55.