Dissociation of Tris(triphenylphosphine)chlororhodium(I) in Solution

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Summary The equilibrium constant for the dissociation of $RhCl(PPh_3)_3$ according to the reaction, $RhCl(PPh_3)_3 \rightleftharpoons RhCl(PPh_3)_2 + PPh_3$, has been determined spectrophotometrically to be $(1{\cdot}4 \pm 0{\cdot}4) \times 10^{-4}$ M in benzene solution at 25°.

THE dissociation of $RhCl(PPh_3)_3$ in solution [into $RhCl(PPh_3)_2$ and PPh_3] has been a subject of considerable interest and controversy, particularly in view of the indications of the importance of such dissociation to the distinctive chemical properties of $RhCl(PPh_3)_3$, *e.g.*, as a hydrogenation catalyst[1] and as a reagent for the decarbonylation of aldehydes.[2] Recent n.m.r. measurements[3] and chemical evidence[4] indicate that the degree of dissociation in solvents such as benzene and chlorinated hydrocarbons is much smaller than suggested by early molecular-weight measurements,[1] but fail to yield quantitative estimates of such dissociation. Clarification of this situation is afforded by the results of the spectrophotometric measurements which we report here and which lead to a quantitative determination of the equilibrium constant, *K*, for the dissociation of $RhCl(PPh_3)_3$ in benzene solution according to equation 1.

$$RhCl(PPh_3)_3 \overset{K}{\rightleftharpoons} RhCl(PPh_3)_2 + PPh_3 \qquad (1)$$

Dilute benzene solutions of $RhCl(PPh_3)_3$ ($< 10^{-3}$ M), from which oxygen had been rigorously excluded, exhibited departures from Beers' law, the apparent extinction co-*efficient in* the 350—500 nm range *decreasing* with increasing dilution. Addition of an excess of PPh_3 resulted in the restoration of the absorbance to the limiting spectrum characteristic of concentrated ($> 10^{-3}$ M) solutions of $RhCl(PPh_3)_3$. The effect of PPh_3 on the spectrum, depicted in Figure 1, was found to be quantitatively in accord with the dissociation reaction (1) which is described by the equilibrium relations (2), where A is the solution absorbance, A_∞ is the limiting absorbance at high PPh_3 concentrations, ϵ_1 and ϵ_2 are the extinction coefficients of $RhCl(PPh_3)_3$ and $RhCl(PPh_3)_2$, respectively, $\Delta\epsilon = \epsilon_1 - \epsilon_2$, and $[PPh_3]_0$ is the concentration of added (*i.e.*, excess) PPh_3.†

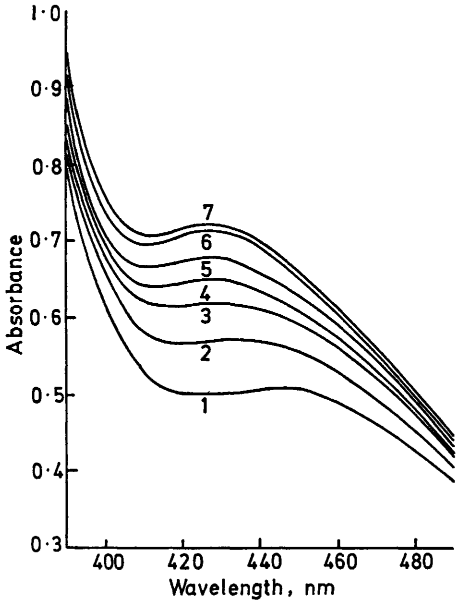

FIGURE 1. *Effect of added* PPh_3 *on the spectrum of* $5{\cdot}1 \times 10^{-4}$ M $RhCl(PPh_3)_3$ *in benzene* (1 cm *light path*). *Added* PPh_3, M: 1, 0·0; 2, $2{\cdot}5 \times 10^{-4}$; 3, $5{\cdot}0 \times 10^{-4}$; 4, $7{\cdot}5 \times 10^{-4}$; 5, $12{\cdot}5 \times 10^{-4}$; 6, 25×10^{-4}; 7, $> 5 \times 10^{-3}$ (= A_∞).

$$K = \frac{[RhCl(PPh_3)_2][PPh_3]}{[RhCl(PPh_3)_3]} = \frac{[A_\infty - A]\{[PPh_3]_0\Delta\epsilon + [A_\infty - A]\}}{\Delta\epsilon\{A - A_\infty[1 - \Delta\epsilon/\epsilon_1]\}} \qquad (2)$$

Fitting the spectral data to equation (2), demonstrated by Figure 2, yielded the value $K = (7 \pm 1) \times 10^{-5}$ M, which was found to be independent of the wavelength over the range 400—420 nm where the absorbance changes permit the most accurate determinations of K. It should be noted that this value of K is sufficiently small to support the conclusions derived from other measurements[3,4] that dissociation of $RhCl(PPh_3)_3$ in more concentrated solutions ($> 10^{-2}$ M) is not extensive.‡

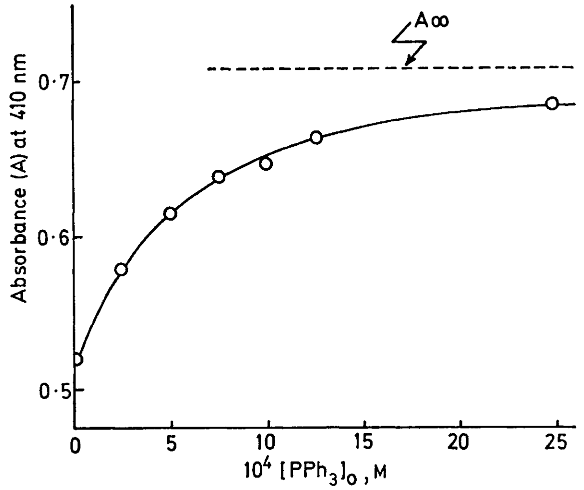

FIGURE 2. *Effect of added* PPh_3 *on the absorbance at* 410 nm *of a* $5{\cdot}1 \times 10^{-4}$ M $RhCl(PPh_3)_3$ *solution in benzene. The circles are experimental points (from Figure* 1). *The solid curve is computed from equation* (2) *using* $\epsilon_1 = 1{\cdot}42 \times 10^3$, $\epsilon_2 = 0{\cdot}42 \times 10^3$ *and* $K = 1{\cdot}4 \times 10^{-4}$M.

Preliminary analogous measurements on $PhBr(PPh_3)_3$ and $RhI(PPh_3)_3$ yielded similar values of *ca.* 10^{-4}M in each case for the corresponding dissociation equilibrium constants in benzene at 25°.

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† The derivation of equation (2) is based on the valid assumption that, compared with those of $RhCl(PPh_3)_3$, and $RhCl(PPh_3)_2$ the extinction coefficient of PPh_3 over the wavelength range of the measurements, 390—440 nm, is negligible. All absorbance values refer to 1 cm light path.

‡ Within the accuracy of the fit of our experimental data to equation (2), no contribution from the accompanying dimerization process,[1] $2RhCl(PPh_3)_2 \rightleftharpoons [RhCl(PPh_3)_2]_2$, could be detected.

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