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## Dissociation of Tris(triphenylphosphine)chlororhodium(1) in Solution

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Summary The equilibrium constant for the dissociation of RhCl(PPh<sub>3</sub>)<sub>3</sub> according to the reaction, RhCl(PPh<sub>3</sub>)<sub>3</sub>  $\rightleftharpoons$  RhCl(PPh<sub>3</sub>)<sub>2</sub> + PPh<sub>3</sub>, has been determined spectrophotometrically to be  $(1.4 \pm 0.4) \times 10^{-4}$  M in benzene solution at 25°.

THE dissociation of RhCl(PPh<sub>3</sub>)<sub>3</sub> in solution [into RhCl-(PPh<sub>3</sub>)<sub>2</sub> and PPh<sub>3</sub>] 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<sub>3</sub>)<sub>3</sub>, *e.g.*, as a hydrogenation catalyst<sup>1</sup> and as a reagent for the decarbonylation of aldehydes.<sup>2</sup> Recent n.m.r. measurements<sup>3</sup> and chemical evidence<sup>4</sup> indicate that the degree of dissociation in solvents such as benzene and chlorinated hydrocarbons is much smaller than suggested by early molecularweight measurements,<sup>1</sup> 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<sub>3</sub>)<sub>3</sub> in benzene solution according to equation 1.

$${}^{K}_{\mathrm{RhCl}(\mathrm{PPh}_{3})_{3}} \rightleftharpoons \mathrm{RhCl}(\mathrm{PPh}_{3})_{2} + \mathrm{PPh}_{3} \tag{1}$$



FIGURE 1. Effect of added PPh<sub>3</sub> on the spectrum of  $5.1 \times 10^{-4}$  M RhCl(PPh<sub>3</sub>)<sub>3</sub> in benzene (1 cm light path). Added PPh<sub>3</sub>, 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,  $25 \times 10^{-4}$ ; 7,  $> 5 \times 10^{-3}$  (= A<sub>∞</sub>).

the dissociation reaction (1) which is described by the equilibrium relations (2), where A is the solution absorbance,  $A_{\infty}$  is the limiting absorbance at high PPh<sub>3</sub> concentrations,  $\epsilon_1$  and  $\epsilon_2$  are the extinction coefficients of  $\mathrm{RhCl}(\mathrm{PPh}_3)_3$  and  $\mathrm{RhCl}(\mathrm{PPh}_3)_2$ , respectively,  $\Delta \epsilon = \epsilon_1 - \epsilon_2$ , and  $[PPh_3]_0$  is the concentration of added (*i.e.*, excess) PPh3.†

## [RhCl(PPh<sub>3</sub>)<sub>2</sub>][PPh<sub>3</sub>] K =[RhCl(PPh<sub>3</sub>)<sub>3</sub>] $\frac{[A_{\infty} - A] \{ [PPh_3]_0 \Delta \epsilon + [A_{\infty} - A] \}}{\Delta \epsilon \{ A - A_{\infty} [1 - \Delta \epsilon / \epsilon_1] \}}$ (2)

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Fitting the spectral data to equation (2), demonstrated by Figure 2, yielded the value  $K = (7 \pm 1) \times 10^{-5}$  M,



FIGURE 2. Effect of added PPh<sub>3</sub> on the absorbance at 410 nm of a  $5\cdot 1 \times 10^{-4}$  M RhCl(PPh<sub>3</sub>)<sub>3</sub> solution in benzene. The circles are experimental points (from Figure 1). The solid curve is computed from equation (2) using  $\epsilon_1 = 1.42 \times 10^3$ ,  $\epsilon_2 = 0.42 \times 10^3$  and K  $= 1.4 \times 10^{-4} \text{m}.$ 

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<sup>3,4</sup> that dissociation of RhCl(PPh<sub>3</sub>)<sub>3</sub> in more concentrated solutions  $(> 10^{-2} \text{ M})$  is not extensive.<sup>‡</sup>

Preliminary analogous measurements on PhBr(PPh<sub>3</sub>)<sub>3</sub> and  $RhI(PPh_3)_3$  yielded similar values of ca. 10<sup>-4</sup>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 tinction coefficient of  $PPh_3$  over the wavelength range of the measurements, 390–440 nm, is negligible. All absorbance values extinction coefficient of PPh<sub>3</sub> over the wavelength range of the measurements, 390-440 nm, is negligible. refer to 1 cm light path.

t Within the accuracy of the fit of our experimental data to equation (2), no contribution from the accompanying dimerization  $\operatorname{process}^{1} 2\operatorname{RhCl}(\operatorname{PPh}_{3})_{2} \rightleftharpoons [\operatorname{RhCl}(\operatorname{PPh}_{3})_{2}]_{2}, \text{ could be detected.}$ 

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