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APPENDIX I

Preparation of Thallium (III) Chloride(5) ($TlCl_3$)

Thallium (III) chloride was prepared by passing dry chlorine gas through a suspension of 9.6 g (0.04 mole) of thallium (I) chloride in dry acetonitrile until a clear solution was obtained. Excess chlorine gas was removed by the passage in a dry nitrogen gas from the solution for 15 minutes, after which the solvent was evaporated to dryness under reduced pressure, left behind the white, needle crystalline product. This compound is alway used as a solution in dry ether.

Preparation of Phenylmagnesium Bromide(53) (PhMgBr)

Equip a 250 cm^3 round-bottomed flask with a reflux condenser (preferably of the double surface type) and a calcium chloride tube, it is important that the apparatus should be thoroughly dry. Place 3.2 g. (0.13 mole) of dry magnesium turnings, a small crystal of iodine, 7.0 g. (5 cm^3, 0.05 mole) of dry bromobenzene and 10 cm^3 of sodium-dried ether in the flask. If the magnesium does not react within a few minutes, warm the flask on a water bath so that the ether refluxes gently and then remove the bath. This will generally start the reaction. The formation of the Grignard reagent will be indicated by the disappearance of the iodine colour, the production of a cloudiness, and the gently boiling of the ether. Replace the guard tube by a separatory funnel containing a solution of 17 g. (12 cm^3, 0.10 mole) of dry bromobenzene in 70 cm^3 of anhydrous ether and carrying a calcium chloride guard tube in its mounth. Run this solution slowly into the flask at such a rate that the ether boils gently from the heat of reaction alone without the application of external heating. This operation occupies about 30 minutes. Replace the separatory funnel by the guard tube and reflux the mixture gently on a water bath for 30 minutes in order to complete the reaction. The solution will now be either cloudy or slightly dark in colour. The resulted phenylmagnesium bromide can react readily with thallium (III) chloride or mercury (II) bromide to yield diphenylthallium bromide and phenylmercury bromide respectively.

APPENDIX II

Calculation of the Formation Constant (Kf) of the Complexes.(54)

The experimental plot for the 1:1 complex shown in Figure 4.6 can be analyzed as follows.

Suppose that the total concentration of the organometallic compound is [M]. then that of the ligand at the end point will also be [M] . If the reaction between M and L at this point were complete, the concentration of the complex, [ML] would be C, and its absorbance would be the same as the absorbance Am measured in the presence of a very large excess of L that the dissociation of the complex is virtually completely repressed. Actually however, the formation of the complex is not quite complete at the "end point" and so the absorbance A at that point is smaller than Am. Therefore,

$$\frac{[ML]}{C} = \frac{A}{Am} \qquad (1)$$

$$[ML] = \frac{A}{Am} C \qquad (2)$$

and $$[M] = [L] = C - [ML] \qquad (3)$$

From which the formation constant of the complex is

$$Kf = \frac{[ML]}{[M][L]} \qquad (4)$$

Here, the phenanthroline-Ph_2TlBr system will be cited as an example to illustrate the calculation of the Kf by the method described above. As has been shown in the text that the experiment involved the preparation and the measurement of the ML absorbance of a number of mixture containing 1.200 x 10^{-5} mol l^{-1} of 1,10 - phenanthroline [L] and varying concentration of Ph_2TlBr [M]. At the end point of the molar ratio plots in Figure 4.6 (a), it is found that the concentration of M is 1.200 x 10^{-5} mol l^{-1}. The maximum absorbance approaches a constant value of 1.080 in the presence of a large excess of M, and that the absorbance of a solution containing 1.200 x 10^{-5} mol l^{-1} is 0.842. From these data it follows immediately that the formula of the complex is ML. In the solution containing 1.200 x 10^{-5} mol l^{-1} L, the calculation gives,

$$[ML] = \frac{0.842}{1.080} \times 1.200 \times 10^{-5}$$

$$= 0.936 \times 10^{-5}\ \text{mol}\ l^{-1}$$

From equation (3), the concentration of M and L are obtained

$$[M] = 1.200 \times 10^{-5} - 0.936 \times 10^{-5} = 0.264 \times 10^{-5}\ \text{mol}\ l^{-1}$$

$$[L] = 1.200 \times 10^{-5} - 0.936 \times 10^{-5} = 0.264 \times 10^{-5}\ \text{mol}\ l^{-1}$$

From which Kf is found by equation (4)

$$Kf = \frac{0.936 \times 10^{-5}}{(0.264 \times 10^{-5})^2} \quad \frac{\text{mol}\ l^{-1}}{(\text{mol}\ l^{-1})^2}$$

$$= 1.34 \times 10^{6} \quad \text{mol}^{-1}\ l$$

VITA

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