complex. The infrared spectrum of the clear solution obtained after the complete reaction of $LiAlH_4$ and $AlCl_3$ showed the presence of $LiAlH_4$ and AlH_3 in solution. Elemental analysis of the white solid obtained after complete removal of the solvent corresponds to an empirical formula $LiAl_3H_{10}\cdot 0.81Et_2O$.[8] The x-ray powder diffraction data (Table I) as well as the dta–tga of the solid under static argon atmosphere (Figure 1) indicate that actually it is a physical mixture of $LiAlH_4$ and AlH_3 and not a complex.

In conclusion, we have repeated the work of previous workers[2–6] in exactly the same manner described in the literature. However, we do not find convincing evidence to indicate the existence of $LiAl_2H_7$, $LiAl_3H_{10}$, and $LiAl_4H_{13}$. The difference in x-ray powder diffraction data and dta–tga of the so-called "$LiAlH_4$–AlH_3" complexes reported by previous workers may be due to the isolation of solids with different degrees of solvation than the $LiAlH_4$ and AlH_3 to which they were compared. In addition we now know that ether cleavage of $AlH_3\cdot OEt_2$ occurs during the dta–tga heating process resulting in the formation of hydridoaluminum alkoxides. These alkoxides decompose at temperatures different from those of $LiAlH_4$ and AlH_3, possibly giving misleading information that complexes are present.

Our work is not to be interpreted to mean that complexes of $LiAlH_4$ and AlH_3 do not exist or that they have not been prepared by previous workers in this area. Our report is only that *we* have not been able to find evidence of such complexes after considerable effort to do so.

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Registry No. $LiAlH_4$, 16853-85-3; AlH_3, 7784-21-6; LiH, 7580-67-8; $AlCl_3$, 7446-70-0; $LiAl_2H_7$, 12258-28-5; $LiAl_3H_{10}$, 23065-75-0; $LiAl_4H_{13}$, 12330-41-5.

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Formation Constant of $Pd(CN)_4^{2-}$

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Sir:

Two potentiometric studies of $Pd(CN)_4^{2-}$ using palladium metal electrodes are reported in the literature,[1,2] which give log β_4 for this complex as 51.6[1] and 42.4.[2] In addition, log K_5 has been reported as 2.9,[2] and a value of $\Delta H_{\beta_4} = -92.3$ kcal mol^{-1} was determined[2] calorimetrically. Apart from the disparity between them, these log β_4 values seem rather low. For example, combining the reported enthalpy change on complex formation with the two formation constants gives entropies of −74[1] and −116 gibbs mol^{-1},[2] which is very much more unfavorable than could be expected from the entropy change on complex formation of other similar cyanide complexes, e.g., $Hg(CN)_4^{2-}$ with $\Delta S_{\beta_4} = -34$ gibbs mol^{-1} and $Ni(CN)_4^{2-}$ with $\Delta S_{\beta_4} = -7$ gibbs mol^{-1}.

In order to resolve the above disparity, we decided to carry out a potentiometric study using a palladium metal electrode. As discussed below, the potentials measured were meaningless in relation to the formation constant of $Pd(CN)_4^{2-}$. An indication that log β_4 was very large, larger than 60, was, however, obtained. All techniques for measuring stability constants involve a competition reaction of some kind. A stability constant such as that for $Pd(CN)_4^{2-}$ presents a rather unusual problem, since the complex is not easily broken down. Thus, a glass-electrode study could not be used, since, with log β_4 greater than 60, the proton will not be able to remove cyanide from the complex to any great extent. However, if the equilibrium is studied in the presence of a second ligand, such as chloride, the cyanide ion is competing with chloride rather than with water for coordination to the palladium(II) ion. Since chloride has very little affinity for the proton, the presence of the chloride ion will enable the proton to compete with the palladium(II) ion more effectively for the available cyanide. In this type of competition reaction one measures the reaction constant for

$$PdCl_4^{2-} + 4HCN \rightleftharpoons Pd(CN)_4^{2-} + 4H^+ + 4Cl^-$$

This reaction constant is then combined with the formation constant of $PdCl_4^{2-}$, which we have measured to be 11.0 using a palladium metal electrode, to give the formation constant of $Pd(CN)_4^{2-}$. We decided to use uv spectroscopy to monitor the equilibrium concentrations of $PdCl_4^{2-}$ and $Pd(CN)_4^{2-}$ as functions of pH and HCN and Cl^- concentrations and thereby to calculate the formation constant of $Pd(CN)_4^{2-}$.

Experimental Work. All reagents used were of reagent grade. The concentration of palladium in the solutions was checked analytically. The cell and accompanying equipment for making the potentiometric study are described elsewhere.[3] Uv spectra were recorded using a Beckmann Acta CIII recording spectrophotometer. Kinetic runs were carried out at 25 °C.

Results and Discussion. (a) Potentiometry. Potentials, which were not very reproducible, were obtained with different CN^- to $Pd(CN)_4^{2-}$ ratios. The potentials were sensitive to stirring speed, indicating that they were not equilibrium potentials but were mixed potentials resulting from some reaction taking place at the electrode. The uv spectra of the solutions indicated a slow increase of $Pd(CN)_4^{2-}$ concentration with time, showing that the reaction was the dissolution of palladium by cyanide. Tests using an oxygen electrode showed that the initial concentration of oxygen was less than 0.01 ppm, which could not account for the quantity of palladium dissolved. It therefore seemed likely that the dissolution of palladium was taking place with hydrogen evolution

$$Pd(s) + 2H^+ + 4CN^- \rightarrow Pd(CN)_4^{2-} + H_2(g)$$

This reaction should be sensitive to pH, so that, in order to minimize its contribution, the pH was taken up from 9, the natural pH of the solutions, to 12. Even here sensitivity to stirring speed was observed, although a much slower dissolution rate was found. With prolonged exposure to these solutions, the palladium wire became pH sensitive, indicating that it had absorbed sufficient hydrogen to act as a hydrogen electrode. Therefore, it would seem that the potentials observed by previous workers[1,2] were also not equilibrium potentials and that the stability constants reported by them are in error. The fact that the evolution of hydrogen took place in the solutions which we studied puts a lower limit on log β_4 for $Pd(CN)_4^{2-}$

of about 60.

(b) Spectroscopy. Several reactions were investigated as possible suitable competition reactions, but, apart from the Cl^- vs. CN^- reaction, all failed for one or another reason. For example, with I^- and CN^-, the formation of highly colored I^{3-} on standing with the long equilibration times required meant that uv spectroscopy was useless for following the reaction. As might have been expected, the reaction of $Pd(CN)_4^{2-}$ with HCl and the reaction of $PdCl_4^{2-}$ with HCN produced intermediate complexes. The same three complexes, which we shall call A, B, and C, appeared in both reaction sequences, so that one may tentatively assign the reactions to

$$\mathrm{PdCl_4}^{2-} \underset{\mathrm{HCl}}{\overset{\mathrm{HCN}}{\rightleftharpoons}} \underset{\mathrm{A}}{\mathrm{PdCl_3CN}^{2-}} \underset{\mathrm{HCl}}{\overset{\mathrm{HCN}}{\rightleftharpoons}} \underset{\mathrm{B}}{\mathrm{PdCl_2(CN)_2}^{2-}} \underset{\mathrm{HCl}}{\overset{\mathrm{HCN}}{\rightleftharpoons}}$$
$$\underset{\mathrm{C}}{\mathrm{PdCl(CN)_3}^{2-}} \underset{\mathrm{HCl}}{\overset{\mathrm{HCN}}{\rightleftharpoons}} \mathrm{Pd(CN)_4}^{2-}$$

The pseudo-first-order rate constant for the formation of B from $PdCl_4^{2-}$ was some 10^2 times higher than the constant for further reaction to form C, while, for the reverse reactions, the rate of reaction of B with HCl to form A was some 10^3 times slower than the reaction of C to form B, suggesting very strongly that B was the deactivated trans isomer. Presumably when the cis isomer is formed in the reaction of C with HCl, it rearranges very rapidly to form the trans, since it is not observed. An extensive kinetic study was carried out on these reactions in the hope of combining the forward and reverse rates to obtain values of the individual log K_n values. This was, however, abandoned as part of the formation constant study, since the number of reaction paths was too great to be useful in this way, so that the kinetic results will not be reported here.

From a stability constant point of view, the fact that these reactions could take place at all in fairly strong HCl meant that log β_4 was very much larger than previously reported. For example, in 8.4×10^{-4} M HCN and 0.38 M HCl, 10^{-4} M $PdCl_4^{2-}$ reacts completely to form $Pd(CN)_4^{2-}$. After complete reaction, 4.4×10^{-4} M HCN will be left. The pK_a of HCN is 9.2, which means that in 0.38 M HCl and 4.4×10^{-4} M HCN the free cyanide concentration will be 7.3×10^{-13} M. If we estimate that in the latter solution we could have detected 0.1% of unreacted $PdCl_4^{2-}$—at 278 nm the extinction coefficient of $PdCl_4^{2-}$ is 12000, while that of $Pd(CN)_4^{2-}$ is 170—this puts a lower limit on log β_4 for $Pd(CN)_4^{2-}$ of 61. Similarly, in 9 M HCl, $Pd(CN)_4^{2-}$ reacted to produce some $PdCl_4^{2-}$, but mainly intermediate species, after a period of 3 months. The intermediate species all have much lower intensity spectra at 278 nm than does $PdCl_4^{2-}$. If we assumed that the observed absorbance was due to a mixture of $PdCl_4^{2-}$ and $Pd(CN)_4^{2-}$ only, this gave an upper limit to log β_4 of about 65. The mean of the upper and lower limits set by these and many other similar experiments gives a value for log β_4 for $Pd(CN)_4^{2-}$ of about 63. This now gives a much more realistic value for the entropy change on complex formation, ΔS_{β_4}, using the reported[2] calorimetrically determined enthalpy change, of -21 gibbs mol^{-1}.

In dilute HCl (less than 2 M), solutions of $Pd(CN)_4^{2-}$ will, after a few days, precipitate out small quantities of $Pd(CN)_2$. After completion of the reaction, so that the solutions are once more clear, the residual $Pd(CN)_4^{2-}$ can be determined spectrophotometrically. A value of log K_{s4}, corresponding to the equilibrium

$$\mathrm{Pd(CN)_2(s)} + 2\mathrm{CN}^- \rightleftharpoons \mathrm{Pd(CN)_4}^{2-}\mathrm{(aq)}$$

could then be calculated as 20.8 ± 0.1. Combining the value of log $\beta_4 = 63$ determined above with log K_{s4} gives the solubility product of $Pd(CN)_2$, log $K_{so} = -42$.

In relation to the reported[2] value of log $K_5 = 2.9$ for palladium(II) with cyanide, we have observed the uv spectrum of $Pd(CN)_4^{2-}$ in up to 0.1 M free cyanide and observed no change. It has also been reported[4] that no infrared evidence for the existence of this complex can be obtained. One concludes, therefore, that the log K_5 value reported merely reflected the non-Nernstian behavior of the observed potentials, which is to be expected, since they are not true equilibrium potentials.

We have carried out a spectrophotometric study on the reaction of $PtCl_4^{2-}$ with HCN and established that log β_4 is very much larger than the previously reported[5] value of 41, being between 65 and 75. One must therefore conclude that this potentiometric study suffered from the same sources of error as did the analogous study involving $Pd(CN)_4^{2-}$. It would seem that, for determining very large stability constants, in addition to the usual precautions regarding precision, it is advisable to carry out studies along the lines discussed above to establish whether the measured stability constant fits the observable chemical facts.

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Registry No. $Pd(CN)_4^{2-}$, 15004-87-2; $PdCl_4^{2-}$, 14349-67-8.

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