that this resonance is indicative of an exchange system, since if a paramagnetic Rh(II) species were being formed, its presence in solution would cause a broadening of the former resonance. After 27 hr the two resonances are of similar size, but it is noteworthy that although the initial well-resolved resonance is slowly replaced by this second broad resonance, it does not appear to become involved in the exchange since the resolution of the former peak remains unaffected. It has also been found that although compound **3** shows an ^{1}H nmr spectrum analogous to the trifluoroacetate one, this second complex shows a much more rapid conversion, the broad resonance being of comparable size after about 30 min, and essentially complete conversion occurs after 20 hr. This observation of the rapid growth of a broad resonance in the ^{1}H nmr shows that care should be taken in the interpretation of such spectra.

Although we have been unable to characterize compound **2**, it is significant that we have been able to obtain the trifluoroacetate hydride in 73% yield from this compound, and, in addition, by reaction with ammonium hexafluorophosphate, the complex $[(POMePh_2)_4Rh]PF_6$ (mp 170°; conductivity in nitrobenzene 22.8 ohm^{-1} cm^2 mol^{-1}) has been obtained in 79% yield. This high yield suggests the reaction is not a disproportionation reaction of the tris compound and implies that this initial compound may be a tetrakisphosphine complex, although we cannot discount the possibility that there is free methoxydiphenylphosphine present in the material. Because of the air sensitivity of the material we have been unable to obtain useful conductivity data but it appears unlikely that compound **2** is $(POMePh_2)_4Rh^+Cl^-$ because the chloro group remains coordinated after protonation with trifluoroacetic acid.

We have been unable to isolate the corresponding complex from *n*-butoxydiphenylphosphine, but since the addition of trifluoroacetic acid to a solution of the compound obtained from chlorodicarbonylrhodium(I) and the phosphine ligand shows a high-field ^{1}H nmr spectrum virtually identical with that found for compound **1**, it is likely that the compound exists in solution.

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Acid–Base Properties of the Systems $AlCl_3$–MCl (M = Li, Na, K, Cs)

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We have recently reported[2] the values of the equilibrium constant for the dissociation $2AlCl_4^- \rightleftarrows Cl^- + Al_2Cl_7^-$ in molten $AlCl_3$–NaCl in the temperature range 175–400°. We now have extended these potentiometric measurements to other $AlCl_3$–MCl (M = Li, K, Cs) systems and report the results in this note.

Experimental Section

The experimental procedures have been described previously.[2] The Cl^- concentration at the equivalence point of a potentiometric titration curve for a slightly basic $AlCl_3$–MCl melt (M = Li, K, Cs) with $AlCl_3$ was calculated as in ref 2. With this information, the desired equilibrium constant can be readily calculated. Only a narrow composition region near the equivalence point was studied. The electrochemical cells were made from quartz except for the Pyrex membrane separating the reference electrode compartment from the bulk melt. Reagent grade KCl was recrystallized twice from water (deionized and distilled). KCl, LiCl (Baker Analyzed reagent grade), and CsCl (99.9% pure from Alfa Inorganics) were dried in quartz tubes under reduced pressure ($\sim 2 \times 10^{-2}$ Torr) at ~400° for several hours; the tubes were then sealed and stored in the drybox.

In the measurements, particular care was taken to make sure that the asymmetry potential[2] was constant with time and temperature. In order to obtain equilibrium between the Pyrex membrane and the melts, the cell was kept at a constant temperature until there was no change in the measured voltage; this was followed by several temperature excursions until the potentials were reproducible to ±3 mV. At the end of each run, the asymmetry potentials were evaluated and corrected for by using saturated solutions of MCl in both compartments.

Results and Discussion

p*K* (where $K = X_{Cl^-}X_{Al_2Cl_7^-}/X_{AlCl_4^-}{}^2$) values at several temperatures are given in Table I. Data for the $AlCl_3$–NaCl system were reported previously.[2] It is obvious that the nature of the cation plays an important role in determining the p*K* value. The greater the polarizing power of the cation, the smaller is the p*K* at a given temperature. Plots of p*K* *vs.* either $1/r$ (where r is the cationic radius) or the cationic size (r^3) were, however, not linear. It is interesting to note that good linearity was obtained for the plot of p*K* *vs.* d^2 (where d is the sum of the radii of M^+ and $AlCl_4^-$). At this time it appears that no theoretical significance may be attached to this correlation.

TABLE I
p*K* VALUES FOR $AlCl_3$–MCl SYSTEMS

Temp, °C	Li^+	Na^+	K^+	Cs^+
175	4.3	7.1		
250	4.0	6.3		
275			7.5	
300	3.9	5.7	7.1	
350	3.8	5.3	6.4	
400	3.8	5.0	5.8	7.4
450				6.8

From the linear plots of p*K* *vs.* $1/T$ for $AlCl_3$–LiCl (the lowest three temperatures), $AlCl_3$–NaCl, and $AlCl_3$–KCl, the ΔH's were calculated to be 4.0, 13.6, and 22.9 kcal/mol, respectively.

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Raman Intensity Measurements on and Boron–Halogen Bond Polarizability Derivatives for the Boron Trihalides

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The observed intensity of a Raman band is given by the expression