of the competition ratio for CO dissociation in substitution reactions with neutral ligands are about 1.0.[20-23] Thus $[Co(CO)_4]^-$ is very efficient at trapping the intermediate $[Co(CO)_2(PPh_3)_2]^+$, probably from being in close proximity.

The necessity for CO dissociation from $[Co(CO)_3(PPh_3)_2]^+$ before reaction with $[Co(CO)_4]^-$ makes it difficult to distinguish a single electron-transfer mechanism from two-electron donation by the $[Co(CO)_4]^-$ to the 16-electron cation, $[Co(CO)_2(PPh_3)_2]^+$. That the final product has PPh_3 substituted on each cobalt indicates that such an acid–base mechanism would be followed by metal–metal bond cleavage, probably homolytic to allow PPh_3 transfer between the cobalt centers. For reactions of $[CpFe(CO)_2]^-$ and $[Mn(CO)_5]^-$ with $[Co(CO)_3(PPh_3)_2]^+$, which occur at rates more rapid than CO dissociation and lead to products that are typical of 17-electron species,[18] a second path must be available for the electron transfer, most likely a single-electron transfer. While at this point, there is no direct evidence regarding the second pathway, that the weak nucleophile, $[Co(CO)_4]^-$, cannot proceed by the second pathway suggests the importance of nucleophilic attack of the carbonyl anion on the carbon of a carbonyl of the cation. The reaction of $[Re(CO)_5(C_2H_4)]^+$ with $[Re(CO)_5]^-$ serves as a model for such nucleophilic attack.[24]

$$[Re(CO)_5(C_2H_4)]^+ + [Re(CO)_5]^- \rightarrow (CO)_5ReC_2H_4Re(CO)_5 \quad (5)$$

Nucleophilic attack at the carbon of carbon monoxide attached to cations has been observed for carbanions and alkoxides and is a plausible step for precursor complex formation. Further work will be necessary to substantiate the possibility of nucleophilic attack for electron transfer in organometallic systems.

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Registry No. $[Co(CO)_3(PPh_3)_2]^+$, 47854-84-2; $[Co(CO)_4]^-$, 14971-27-8; $[Co(CO)_3(PBu_3)]^-$, 22955-42-6; $[Mn(CO)_5]^-$, 14971-26-7; $[CpFe(CO)_2]^-$, 12107-09-4; CO, 630-08-0.

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Aspects of the Chemistry of Water in Ambient-Temperature Chloroaluminate Ionic Liquids: ^{17}O NMR Studies

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Room-temperature ionic liquids composed of mixtures of $AlCl_3$ and organic chloride salts, RCl (R = *N*-(1-butyl)pyridinium cation ($Bupy^+$) or 1-ethyl-3-methylimidazolium cation (Im^+)), have been used as solvents for a wide variety of chemical studies.[1] These molten salts have several desirable properties, including a high chloride ion activity for basic (excess RCl) melt compositions, high Lewis acidity, and nearly aprotic conditions. However, the residual protons present in the melt have been found to have significant effects on the chemistry of certain solutes.[2-4]

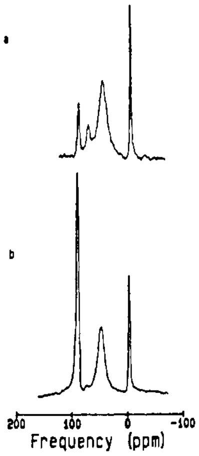

Figure 1. ^{17}O NMR spectra of 50 mM solutions of H_2O in (a) a 1.2:1.0 melt and (b) a 1.73:1.0 melt ($AlCl_3$/ImCl).

The primary source of protonic impurities in the room-temperature chloroaluminate melts is water associated with the organic chloride component of the melts. The latter salts are extremely hygroscopic, and it has proven extremely difficult to remove water completely. Associated with the protonic impurities in the melts is oxide from water and additionally from impurities in $AlCl_3$. Since these impurities are nearly always present in the melts, it is important to understand their chemistry in chloroaluminate media.

Initial studies of oxide in room-temperature melts were concerned with the development of a titration procedure for the determination of oxide impurities in melts.[5,6] It was found that Ti(IV) exhibited two voltammetric reduction waves. These were shown to be due to the reduction of the hexachlorotitanate anion and to the oxotetrachlorotitanate anion. A voltammetric procedure for oxide determination was developed. Surprisingly, the addition of water to a solution of Ti(IV) with a known oxide content shifted the equilibrium between $TiCl_6^{2-}$ and $TiOCl_4^{2-}$ away from the oxochloro complex.[5] This was believed to be due to the formation of an Al–OH-containing species that is unreactive with the hexachloro complex. Subsequent infrared work indicated that an –OH moiety is indeed formed upon addition of water to both basic and acidic melts.[7]

A study of the reduction of protons on a Pt electrode in melts has been reported.[8] The limiting currents for proton reduction increased in a roughly linear fashion with the concentration of water added to basic melts. Less current was observed for an equivalent amount of water added to an acidic melt. Finally, the addition of water to nearly neutral melts apparently results in a release of 2 protons per water molecule.[9]

As part of an ongoing effort to study the chemistry of water in the room-temperature chloroaluminate melts, we have used ^{17}O NMR spectra of water added to the melt to obtain information on the speciation of oxide and protons. This is a preliminary report of our findings, which enable a qualitative description of the nature of the species formed.

Experimental Section

The preparation, purification, and handling of melt components and solutions are fully described elsewhere.[10] Water enriched to 20 or 30%

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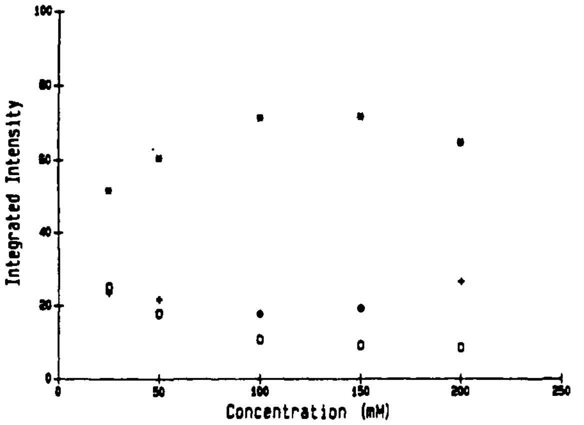

Figure 2. Plot of relative intensities (integrated intensity for the peak divided by total integrated intensity expressed in arbitrary units) for the three peaks as a function of water concentration in a 1.2:1.0 $AlCl_3$/ImCl melt: (*) peak A (49.7 ppm); (+) peak B (73.8 ppm); (O) peak C (91.8 ppm).

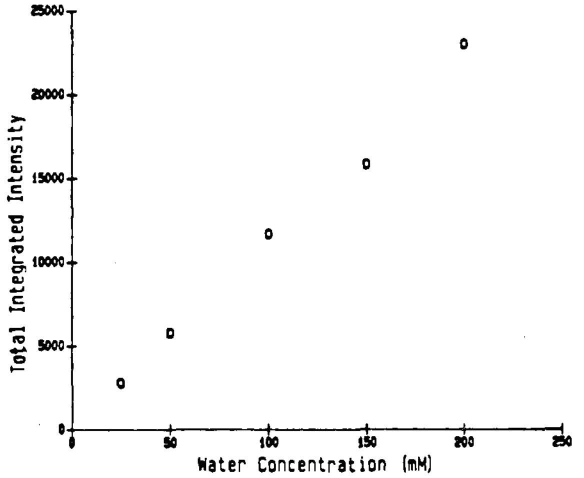

Figure 3. Plot of total integrated intensity (sum of integrated intensities expressed in arbitrary units for individual peaks in spectrum) as a function of the concentration of water added to a 1.2:1.0 $AlCl_3$/ImCl melt.

^{17}O was obtained from Cambridge Isotope Labs and was used as received. $MeEtImDCl_2$ was synthesized in the same manner as $MeEtImHCl_2$,[11] with DCl substituted for HCl.

^{17}O NMR spectra were measured by using a JEOL FX-270 NMR spectrometer operating at 36.54 MHz. The parameters used for typical ^{17}O measurements were as follows: 90° tip angle, 10 000-Hz spectral width, 0.205-s acquisition time, and a 50-μs preacquisition delay time. Proton decoupling was carried out by using broad-band, pseudorandom noise decoupling. All spectra were obtained at 90 °C since base line resolution of all spectral lines could be obtained at this temperature. The ^{17}O signal from unlabeled water in a coaxial tube was used as a reference and assigned a value of 0 ppm. This signal is shown in Figures 1 and 4.

Results and Discussion

^{17}O NMR spectra of solutions of water in acidic melts consist (generally) of three peaks as shown in Figure 1. The relative intensities of these peaks vary as functions of both composition (Figure 1) and concentration (Figure 2). The ^{17}O signal from unlabeled water is shown at 0 ppm. As the melt is made more acidic, resulting in an increase in the mole ratio of $AlCl_3$ to ImCl, the peak furthest downfield (peak C) increases in relative intensity. The peak at 49.7 ppm (peak A) is the most intense peak in the spectrum in melts less acidic than approximately 1.5:1.0. The intensity of peak at 73.8 ppm (peak B) decreases markedly as the melt composition is made more acidic and is nearly negligible beyond a mole ratio of roughly 1.5:1.0.

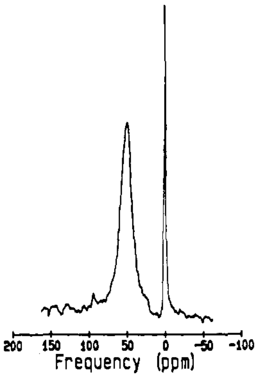

Figure 4. Spectrum of the solution from Figure 1a after HCl is bubbled through it.

Figure 3 is a plot of the total integrated intensity of the three ^{17}O lines observed in a 1.2:1.0 melt with various concentrations of H_2O added. A linear fit to these points has a slope of 112.1 arbitrary units/0.1 mM, an intercept of 65.3 arbitrary units, and a correlation coefficient of 0.997. The linearity of the plot with the concentration of water implies that peaks A–C account for all of the ^{17}O-labeled water added. As the water concentration is increased, the relative intensity of peak A increases sharply while that of peak B increases gradually with concentration. The relative intensity of peak C decreases as the concentration of water is increased.

Addition of H_2O to chloroaluminate melts results in the formation of oxochloroaluminate or hydroxochloroaluminate species. There is but one ^{17}O spectrum reported in the literature for an Al–O complex.[12] Thus, in order to assign the peaks observed to specific solution species, it is necessary to manipulate the chemistry of the system in order to obtain clues concerning the likely nature of the chemical environment of the various ^{17}O sites. The spectrum in Figure 4 is that which results when HCl gas is bubbled through the sample whose spectrum is shown in Figure 1a. Addition of this proton donor results in the disappearance of peaks B and C. This shows that peak A corresponds to oxygen present in a hydroxochloroaluminate species. The constant chemical shift values observed for the peaks as well as the observation of three separate resonances suggest that chemical exchange among the various species is slow on the NMR time scale (the reciprocal of the peak separations in hertz). The highly acidic nature of the medium (the Gutmann AN is roughly 100)[13] leads us to infer that protons and $AlCl_3$ units (from $Al_2Cl_7^-$) compete for oxide sites and that peaks B and C are for oxygen atoms in bridging environments between aluminum atoms. O-bridging oxochloroaluminate species have been proposed for high-temperature chloroaluminate melts[14] and have been shown to exist by crystallographic investigations of inorganic salts formed with the oxochloroaluminate as a counterion.[15] This is further supported by the downfield chemical shift of these two lines relative to peak A, corresponding to the protonated species, and the observed composition dependence of their intensities. In general, electron-withdrawing substituents around an ^{17}O nucleus result in downfield shifts from the unsubstituted parent peak. Thus, an ^{17}O peak will shift downfield when more acidic moieties surround it. This implies that more acidic ligands surround species B than A and still more surround C than B. Finally, no dimeric species with oxygen in an asymmetric environment can be formed in our melts since the peak intensities vary independently with composition and concentration.

Spectra of dissolved ^{17}O-enriched water at several concentrations in a basic melt are shown in Figure 5. In all cases, a single line is observed. However, the position of the peak shifts with increasing water concentration. The effect of bubbling HCl through

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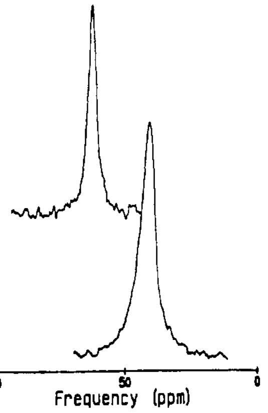

Figure 5. Spectra of water at 50 mM (top) and 200 mM (bottom) concentrations in a 0.8:1.0 melt ($AlCl_3$/ImCl).

a solution of water in a basic melt is to shift the peak upfield. These results suggest that fast chemical exchange is taking place between two or more oxygen environments, probably "Al–O" and "Al–OH" moieties. The "Al–OH" species presumably has a smaller chemical shift value than the "Al–O" species, thus explaining the behavior upon addition of HCl. The observed concentration dependence then indicates that the "Al–O" moiety is the predominant oxide environment at low concentrations while "Al–OH"-containing species are more important at higher concentrations. This suggests that the discrepancy between the infrared[7] and electrochemical[9] results is due to the higher water concentrations used in the former case relative to those typically employed in the neutral-melt amperometric titration technique utilized in the latter case. These results also provide direct evidence for the type of equilibrium used to explain the behavior of the Ti(IV) system upon addition of H_2O. In the latter experiment, relatively large H_2O concentrations were added to the titanium solutions.

In conclusion, ${}^{17}O$ studies have enabled us to deduce the nature of the speciation in H_2O solutions in melts. In acidic melts, three oxygen-containing species are formed: one hydroxochloroaluminate and two O-bridged oxochloroaluminate species. In basic melts, rapid exchange precludes determination of the exact number of species formed, but we can qualitatively conclude that an oxochloroaluminate, probably in a terminal environment, and a hydroxochloroaluminate are present, with the latter species being the predominant form at high water concentrations.

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Registry No. H_2O, 7732-18-5; $AlCl_3$, 7446-70-0; 1-methyl-3-ethylimidazolium chloride, 65039-09-0.

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Rhodium(I) Production during the Oxidation by Water of a Hydrosoluble Phosphine

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Water-soluble and hydrophilic phosphines have been synthesized recently[1–8] to accord water solubility to homogeneous catalysts, affording a means to separate them from organic products in biphasic (water and organic phase) systems. We here report our studies of the highly hydrosoluble trisodium phosphinetriyltri-*m*-benzenesulfonate, TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$, patented by Rhône-Poulenc S.A.[1] We have prepared hydrosoluble rhodium(I) coordination compounds such as $RhCl(TPPTS)_3$ by reacting TPPTS on a Rh(I) precursor under carefully controlled reaction conditions.[9] But attempts to synthetize the persulfonated analogue of Wilkinson's complex from $RhCl_3$ have failed because we have found that this hydrosoluble phosphine is readily oxidized by Rh(III) in water in the absence of oxygen. In this paper we show that a redox process occurs between rhodium(III), TPPTS, and water. The production of phosphine oxide is accompanied by the formation of Rh(I) characterized by its coordination complexes with the sulfonated phosphine.

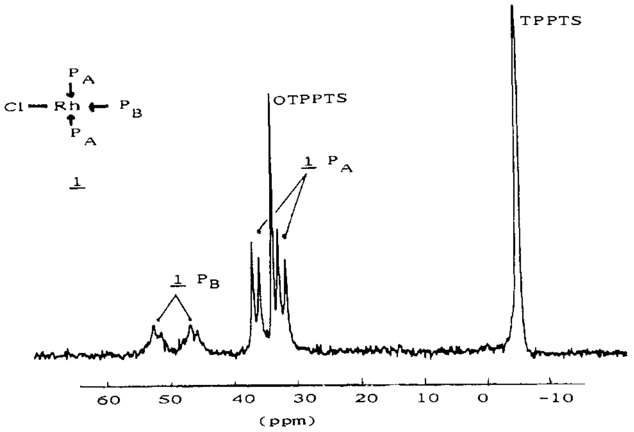

Figure 1. 32.38-MHz ${}^{31}P\{{}^{1}H\}$ NMR spectrum of $RhCl_3 \cdot 3H_2O$ and 3 equiv of TPPTS after 21 h (P_A and P_B = TPPTS).

Table I. ${}^{31}P$ NMR Data in Water

complex	$\delta(P)^{a,b}$	J_{Rh-P}, Hz	$J_{P_A-P_B}$, Hz
1 (H_2O, 36 °C)	34.6 (P_A) 50.7 (P_B)	142 (P_A) 195 (P_B)	39
$RhCl(PPh_3)_3$ (CH_2Cl_2, 28 °C)[10]	32.2 (P_A) 48.9 (P_B)	146 (P_A) 192 (P_B)	38

[a] P_A represents the two equivalent phosphorus atoms trans to each other. P_B is the phosphorus atom trans to the halogen. [b] External reference H_3PO_4 85%.

Results

${}^{31}P$ NMR Studies. When 3 equiv of TPPTS and 1 equiv of $RhCl_3$ are dissolved in scrupulously deaerated water and allowed to react under nitrogen at room temperature, the ${}^{31}P$ NMR spectrum of the reaction mixture recorded after 21 h reveals the presence of $O{=}P(PhSO_3Na)_3$ (OTPPTS), of unreacted phosphine and of $RhCl(TPPTS)_3$ (**1**) (Figure 1).[9] Structure **1** has been assigned by comparison of the data obtained in water with those of the triphenylphosphine complex (Table I).

This experiment demonstrates that rhodium(III) has been partially reduced and trapped by TPPTS (approximately 50% of the rhodium introduced is characterized in the rhodium(I) complex 1) and that oxidation of TPPTS occurs at the same time even in the absence of oxygen. The amount of rhodium(I) and phosphine

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